08-07-00

A

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Joseph D. Lichtenhan, et al. Atty Docket: 38559-257945 (6565-03)

Title: **PROCESS FOR THE FORMATION OF POLYHEDRAL OLIGOMERIC SILSEQUIOXANES**

TRANSMITTAL FOR NEW PATENT APPLICATION

Box Patent Application
Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Enclosed is a new patent application, including:

1. New Application Transmittal (16 pages);
2. Patent application, including 41-page specification (with drawings included), 2 pages of claims, and 1-page abstract;
3. Declaration and Power of Attorney (unsigned); and
4. Postcard for date-stamped confirmation of Patent Office's receipt of these materials.

TYPE OF FILING

☐ This application claims the benefit of an earlier filed U.S. Patent Application under 35 USC 120.

☒ Please accord Applicant the benefit of the priority date of August 4, 1999 to this case pursuant to 35 USC 119. Applicant's claim for priority is based on U.S. Provisional Patent Application Serial No. 60/147,435 filed on said date.

☒ This is an application filed pursuant to 37 CFR 1.53, permitting receipt of a filing date upon filing of specification, claims and drawings, if required, with applicant being given a period of one month from the date of notice to file the fee and oath or declaration.

☒ In the event any parts of this application are incomplete, please treat this as a filing under 37 CFR 1.53 as defined just above.

CERTIFICATE OF MAILING

CERTIFICATE OF MAILING BY "EXPRESS MAIL": I, Janelle Klenk, hereby certify that this correspondence is being deposited with the U. S. Postal Service as Express Mail No. EL618987033US addressed to Box Patent Application, Assistant Commissioner for Patents, Washington, D.C. 20231 on **August 4, 2000**.

Date: Aug. 4, 2000 By: Janelle Klenk

FEE CALCULATION

The filing fee has been calculated as shown below:

		SMALL ENTITY		OTHER THAN A SMALL ENTITY		
BASIC FEE Design Patent		$155	$	$310		$
BASIC FEE Utility Patent		$345	$	$690		$
EXTRA FEES		RATE FEE		RATE FEE		
TOTAL CLAIMS	MINUS 20 =	x 11 =	$	x 22	=	$
INDEP.CLAIMS	MINUS 3 =	x 40 =	$	x 80	=	$
☐ MULTIPLE DEP.CLAIM		+130 =	$	+260	=	$
☐ ASSIGNMENT		+ 40 =	$	+ 40	=	$
☐ RULE 53 SURCHARGE		+ 65 =	$	+130	=	$
TOTAL			$			$

FEE PAYMENT

☐ Attached is Check No. _____ in the sum of $_____ to cover the filing fee.

☐ Please charge Account No. _____ the sum of $_____.

FEE DEFICIENCY

☒ The Commissioner is authorized to charge (or credit any overpayment) to deposit account No. _____:

- ☒ Any additional filing fees required under 37 CFR 1.16, *except Rule 53 filings, which will be paid within the time permitted by PTOL 1533*.
- ☐ Assignment Recordal fees.

☒ The filing fee and surcharge under 37 CFR 1.16, patent application processing fees under 37 CFR 1.17 and patent issue fees under 37 CFR 1.18 are intended to be paid by our firm as they arise. As no abandonment is intended by any inadvertent nonpayment of fees, the Commissioner is hereby authorized to charge payment of such fees as from time to time come due, if not paid prior to due date to our Deposit Account No. _____.

☐ A duplicate copy of this sheet is enclosed.

Respectfully submitted,

Dated: 8-4-00

David H. Jaffer
Reg. No. 32,243

PILLSBURY MADISON & SUTRO
2550 Hanover Street
Palo Alto, California 94304-1115
Phone: (650) 233-4510
Facsimile: (650) 233-4545

Practitioner's Docket No. 38559-257945 (6565-03) **PATENT**

Preliminary Classification:

Proposed Class:

Subclass:

NOTE: "All applicants are requested to include a preliminary classification on newly filed patent applications. The preliminary classification, preferably class and subclass designations, should be identified in the upper right-hand corner of the letter of transmittal accompanying the application papers, for example 'Proposed Class 2, subclass 129.'" M.P.E.P. § 601, 7th ed.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Box Patent Application
Assistant Commissioner for Patents
Washington, D.C. 20231

NEW APPLICATION TRANSMITTAL

Transmitted herewith for filing is the patent application of

Inventor(s): Joseph D. LICHTENHAN, Joseph J. SCHWAB, Yi-Zong AN, William REINERTH, Michael J. CARR, Frank J. FEHER, and Raquel TERROBA

WARNING: *37 C.F.R. § 1.41(a)(1) points out:*

"(a) A patent is applied for in the name or names of the actual inventor or inventors.

"(1) The inventorship of a nonprovisional application is that inventorship set forth in the oath or declaration as prescribed by § 1.63, except as provided for in § 1.53(d)(4) and § 1.63(d). If an oath or declaration as prescribed by § 1.63 is not filed during the pendency of a nonprovisional application, the inventorship is that inventorship set forth in the application papers filed pursuant to § 1.53(b), unless a petition under this paragraph accompanied by the fee set forth in § 1.17(i) is filed supplying or changing the name or names of the inventor or inventors."

For (title): PROCESS FOR THE FORMATION OF POLYHEDRAL OLIGOMERIC SILSESQUIOXANES

CERTIFICATION UNDER 37 C.F.R. § 1.10*
(Express Mail label number is mandatory.)
(Express Mail certification is optional.)

I hereby certify that this New Application Transmittal and the documents referred to as attached therein are being deposited with the United States Postal Service on this date August 4, 2000, in an envelope as "Express Mail Post Office to Addressee," mailing Label Number EL618987033US, addressed to the: Assistant Commissioner for Patents, Washington, D.C. 20231.

Janelle Klenk
(type or print name of person mailing paper)

Janelle Klenk
Signature of person mailing paper

WARNING: *Certificate of mailing (first class) or facsimile transmission procedures of 37 C.F.R. § 1.8 cannot be used to obtain a date of mailing or transmission for this correspondence.*

****WARNING:*** *Each paper or fee filed by "Express Mail" **must** have the number of the "Express Mail" mailing label placed thereon prior to mailing. 37 C.F.R. § 1.10(b).*
*"Since the filing of correspondence under § 1.10 without the Express Mail mailing label thereon is an oversight that can be avoided by the exercise of reasonable care, requests for waiver of this requirement will **not** be granted on petition." Notice of Oct. 24, 1996, 60 Fed. Reg. 56,439, at 56,442.*

1. Type of Application

This new application is for a(n)

(check one applicable item below)

☒ Original (nonprovisional)

☐ Design

☐ Plant

WARNING: ***Do not*** *use this transmittal for a completion in the U.S. of an International Application under 35 U.S.C. § 371(c)(4), unless the International Application is being filed as a divisional, continuation or continuation-in-part application.*

WARNING: ***Do not*** *use this transmittal for the filing of a provisional application.*

NOTE: If one of the following 3 items apply, then complete and attach ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF A PRIOR U.S. APPLICATION CLAIMED and a NOTIFICATION IN PARENT APPLICATION OF THE FILING OF THIS CONTINUATION APPLICATION.

☐ Divisional.

☐ Continuation.

☐ Continuation-in-part (C-I-P).

2. Benefit of Prior U.S. Application(s) (35 U.S.C. §§ 119(e), 120, or 121)

NOTE: A nonprovisional application may claim an invention disclosed in one or more prior filed copending nonprovisional applications or copending international applications designating the United States of America. In order for a nonprovisional application to claim the benefit of a prior filed copending nonprovisional application or copending international application designating the United States of America, each prior application must name as an inventor at least one inventor named in the later filed nonprovisional application and disclose the named inventor's invention claimed in at least one claim of the later filed nonprovisional application in the manner provided by the first paragraph of 35 U.S.C. § 112. Each prior application must also be:

(i) An international application entitled to a filing date in accordance with PCT Article 11 and designating the United States of America; or

(ii) Complete as set forth in § 1.51(b); or

(iii) Entitled to a filing date as set forth in § 1.53(b) or § 1.53(d) and include the basic filing fee set forth in § 1.16; or

(iv) Entitled to a filing date as set forth in § 1.53(b) and have paid therein the processing and retention fee set forth in § 1.21(l) within the time period set forth in § 1.53(f).

37 C.F.R. § 1.78(a)(1).

NOTE: If the new application being transmitted is a divisional, continuation or a continuation-in-part of a parent case, or where the parent case is an International Application which designated the U.S., or benefit of a prior provisional application is claimed, then check the following item and complete and attach ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.

WARNING: *If an application claims the benefit of the filing date of an earlier filed application under 35 U.S.C. §§ 120, 121 or 365(c), the 20-year term of that application will be based upon the filing date of the earliest U.S. application that the application makes reference to under 35 U.S.C. §§ 120, 121 or 365(c). (35 U.S.C. § 154(a)(2) does not take into account, for the determination of the patent term, any application on which priority is claimed under 35 U.S.C. §§ 119, 365(a) or 365(b).) For a c-i-p application, applicant should review whether any claim in the patent that will issue is supported by an earlier application and, if not, the applicant should consider canceling the reference to the earlier filed application. The term of a patent is not based on a claim-by-claim approach. See Notice of April 14, 1995, 60 Fed. Reg. 20,195, at 20,205.*

WARNING: *When the last day of pendency of a provisional application falls on a Saturday, Sunday, or Federal holiday within the District of Columbia, any nonprovisional application claiming benefit of the provisional application* ***must*** *be filed prior to the Saturday, Sunday, or Federal holiday within the District of Columbia. See 37 C.F.R. § 1.78(a)(3).*

☒ The new application being transmitted claims the benefit of prior U.S. application(s). Enclosed are ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.

3. Papers Enclosed

A. Required for filing date under 37 C.F.R. § 1.53(b) (Regular) or 37 C.F.R. § 1.153 (Design) Application

41 Pages of specification

2 Pages of claims

_____ Sheets of drawing (included in specification)

WARNING: ***DO NOT*** *submit original drawings. A high quality copy of the drawings should be supplied when filing a patent application. The drawings that are submitted to the Office must be on strong, white, smooth, and non-shiny paper and meet the standards according to § 1.84. If corrections to the drawings are necessary, they should be made to the original drawing and a high-quality copy of the corrected original drawing then submitted to the Office. Only one copy is required or desired. For comments on proposed then-new 37 C.F.R. § 1.84, see Notice of March 9, 1988 (1990 O.G. 57-62).*

NOTE: "Identifying indicia, if provided, should include the application number or the title of the invention, inventor's name, docket number (if any), and the name and telephone number of a person to call if the Office is unable to match the drawings to the proper application. This information should be placed on the back of each sheet of drawing a minimum distance of 1.5 cm. (5/8 inch) down from the top of the page . . ." 37 C.F.R. § 1.84(c)).

(complete the following, if applicable)

☐ The enclosed drawing(s) are photograph(s), and there is also attached a "PETITION TO ACCEPT PHOTOGRAPH(S) AS DRAWING(S)." 37 C.F.R. § 1.84(b).

☐ formal

☐ informal

B. Other Papers Enclosed

_____ Pages of declaration and power of attorney

1 Pages of abstract

_____ Other

4. Additional papers enclosed

☐ Amendment to claims

☐ Cancel in this applications claims _____ before calculating the filing fee. (At least one original independent claim must be retained for filing purposes.)

☐ Add the claims shown on the attached amendment. (Claims added have been numbered consecutively following the highest numbered original claims.)

☐ Preliminary Amendment

☐ Information Disclosure Statement (37 C.F.R. § 1.98)

☐ Form PTO–1449 (PTO/SB/08A and 08B)

☐ Citations

- ☐ Declaration of Biological Deposit
- ☐ Submission of "Sequence Listing," computer readable copy and/or amendment pertaining thereto for biotechnology invention containing nucleotide and/or amino acid sequence.
- ☐ Authorization of Attorney(s) to Accept and Follow Instructions from Representative
- ☐ Special Comments
- ☐ Other

5. Declaration or oath (including power of attorney)

NOTE: A newly executed declaration is not required in a continuation or divisional application provided that the prior nonprovisional application contained a declaration as required, the application being filed is by all or fewer than all the inventors named in the prior application, there is no new matter in the application being filed, and a copy of the executed declaration filed in the prior application (showing the signature or an indication thereon that it was signed) is submitted. The copy must be accompanied by a statement requesting deletion of the names of person(s) who are not inventors of the application being filed. If the declaration in the prior application was filed under § 1.47, then a copy of that declaration must be filed accompanied by a copy of the decision granting § 1.47 status or, if a nonsigning person under § 1.47 has subsequently joined in a prior application, then a copy of the subsequently executed declaration must be filed. See 37 C.F.R. §§ 1.63(d)(1)-(3).

NOTE: A declaration filed to complete an application must be executed, identify the specification to which it is directed, identify each inventor by full name including family name and at least one given name, without abbreviation together with any other given name or initial, and the residence, post office address and country or citizenship of each inventor, and state whether the inventor is a sole or joint inventor. 37 C.F.R. § 1.63(a)(1)-(4).

NOTE: "The inventorship of a nonprovisional application is that inventorship set forth in the oath or declaration as prescribed by § 1.62, except as provided for in § 1.53(d)(4) and § 1.63(d). If an oath or declaration as prescribed by § 1.63 is not filed during the pendency of a nonprovisional application, the inventorship is that inventorship set forth in the application papers filed pursuant to § 1.53(b), unless a petition under this paragraph accompanied by the fee set forth in § 1.17(i) is filed supplying or changing the name or names of the inventor or inventors." 37 C.F.R. § 1.41(a)(1).

☒ Enclosed (unsigned)

Executed by

(check **all** *applicable boxes)*

- ☐ inventor(s).
- ☐ legal representative of inventor(s). 37 C.F.R. §§ 1.42 or 1.43.
- ☐ joint inventor or person showing a proprietary interest on behalf of inventor who refused to sign or cannot be reached.
  - ☐ This is the petition required by 37 C.F.R. § 1.47 and the statement required by 37 C.F.R. § 1.47 is also attached. See item 13 below for fee.

☐ Not Enclosed.

NOTE: Where the filing is a completion in the U.S. of an International Application or where the completion of the U.S. application contains subject matter in addition to the International Application, the application may be treated as a continuation or continuation-in-part, as the case may be, utilizing ADDED PAGE FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION CLAIMED.

☐ Application is made by a person authorized under 37 C.F.R. § 1.41(c) on behalf of *all* the above named inventor(s).

(The declaration or oath, along with the surcharge required by 37 C.F.R. § 1.16(e) can be filed subsequently).

☐ Showing that the filing is authorized.
(not required unless called into question. 37 C.F.R. § 1.41(d))

6. Inventorship Statement

WARNING: *If the named inventors are each not the inventors of all the claims an explanation, including the ownership of the various claims at the time the last claimed invention was made, should be submitted.*

The inventorship for all the claims in this application are:

☒ The same.

or

☐ Not the same. An explanation, including the ownership of the various claims at the time the last claimed invention was made,

☐ is submitted.

☐ will be submitted.

7. Language

NOTE: An application including a signed oath or declaration may be filed in a language other than English. An English translation of the non-English language application and the processing fee of $130.00 required by 37 C.F.R. § 1.17(k) is required to be filed with the application, or within such time as may be set by the Office. 37 C.F.R. § 1.52(d).

☒ English

☐ Non-English

☐ The attached translation includes a statement that the translation is accurate. 37 C.F.R. § 1.52(d).

8. Assignment

☒ An assignment of the invention to Hybrid Plastics

☐ is attached. A separate ☐ "COVER SHEET FOR ASSIGNMENT (DOCUMENT) ACCOMPANYING NEW PATENT APPLICATION" or ☐ FORM PTO 1595 is also attached.

☒ will follow.

NOTE: "If an assignment is submitted with a new application, send two separate letters-one for the application and one for the assignment." Notice of May 4, 1990 (1114 O.G. 77-78).

WARNING: *A newly executed "CERTIFICATE UNDER 37 C.F.R. § 3.73(b)" must be filed when a continuation-in-part application is filed by an assignee. Notice of April 30, 1993, 1150 O.G. 62-64.*

9. Certified Copy

Certified copy(ies) of application(s)

Country	Appln. No.	Filed
Country	Appln. No.	Filed
Country	Appln. No.	Filed

from which priority is claimed

☐ is (are) attached.

☐ will follow.

NOTE: The foreign application forming the basis for the claim for priority must be referred to in the oath or declaration. 37 C.F.R. § 1.55(a) and 1.63.

NOTE: This item is for any foreign priority for which the application being filed directly relates. If any parent U.S. application or International Application from which this application claims benefit under 35 U.S.C. § 120 is itself entitled to priority from a prior foreign application, then complete item 18 on the ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.

10. Fee Calculation (37 C.F.R. § 1.16)

A. ☐ Regular application

CLAIMS AS FILED				
Number filed		Number Extra	Rate	Basic Fee 37 C.F.R. § 1.16(a) $760.00
Total Claims (37 C.F.R. § 1.16(c))	– 20 =		× $ 18.00	
Independent Claims (37 C.F.R. § 1.16(b))	– 3 =		× $ 78.00	
Multiple dependent claim(s), if any (37 C.F.R. § 1.16(d))			+ $260.00	

☐ Amendment cancelling extra claims is enclosed.

☐ Amendment deleting multiple-dependencies is enclosed.

☐ Fee for extra claims is not being paid at this time.

NOTE: If the fees for extra claims are not paid on filing they must be paid or the claims cancelled by amendment, prior to the expiration of the time period set for response by the Patent and Trademark Office in any notice of fee deficiency. 37 C.F.R. § 1.16(d).

Filing Fee Calculation $_____

B. ☐ Design application ($310.00—37 C.F.R. § 1.16(f))

Filing Fee Calculation $_____

C. ☐ Plant application
($480.00—37 C.F.R. § 1.16(g))

Filing fee calculation $_____

11. Small Entity Statement(s)

☐ Statement(s) that this is a filing by a small entity under 37 C.F.R. § 1.9 and 1.27 is (are) attached.

WARNING: *"Status as a small entity must be specifically established in each application or patent in which the status is available and desired. Status as a small entity in one application or patent does not affect any other application or patent, including applications or patents which are directly or indirectly dependent upon the application or patent in which the status has been established. The refiling of an application under § 1.53 as a continuation, division, or continuation-in-part (including a continued prosecution application under § 1.53(d)), or the filing of a reissue application requires a new determination as to continued entitlement to small entity status for the continuing or reissue application. A nonprovisional application claiming benefit under 35 U.S.C. § 119(e), 120, 121, or 365(c) of a prior application, or a reissue application may rely on a statement filed in the prior application or in the patent if the nonprovisional application or the reissue application includes a reference to the statement in the prior application or in the patent or includes a copy of the statement in the prior application or in the patent and status as a small entity is still proper and desired. The payment of the small entity basic statutory filing fee will be treated as such a reference for purposes of this section." 37 C.F.R. § 1.28(a)(2).*

WARNING: *"Small entity status must not be established when the person or persons signing the . . . statement can **unequivocally** make the required self-certification." M.P.E.P., § 509.03, 6th ed., rev. 2, July 1996 (emphasis added).*

(complete the following, if applicable)

☐ Status as a small entity was claimed in prior application

_____ / _____, filed on _____, from which benefit is being claimed for this application under:

35 U.S.C. § ☐ 119(e),
☐ 120,
☐ 121,
☐ 365(c),

and which status as a small entity is still proper and desired.

☐ A copy of the statement in the prior application is included.

Filing Fee Calculation (50% of **A, B** or **C** above)

$_____

NOTE: Any excess of the full fee paid will be refunded if small entitiy status is established and a refund request are filed within 2 months of the date of timely payment of a full fee. The two-month period is not extendable under § 1.136. 37 C.F.R. § 1.28(a).

12. Request for International-Type Search (37 C.F.R. § 1.104(d))

(complete, if applicable)

☐ Please prepare an international-type search report for this application at the time when national examination on the merits takes place.

13. Fee Payment Being Made at This Time

☒ Not Enclosed

☐ No filing fee is to be paid at this time.
(This and the surcharge required by 37 C.F.R. § 1.16(e) can be paid subsequently.)

☐ Enclosed

☐ Filing fee $ _____

☐ Recording assignment
($40.00; 37 C.F.R. § 1.21(h))
(See attached "COVER SHEET FOR ASSIGNMENT ACCOMPANYING NEW APPLICATION".) $ _____

☐ Petition fee for filing by other than all the inventors or person on behalf of the inventor where inventor refused to sign or cannot be reached
($130.00; 37 C.F.R. §§ 1.47 and 1.17(i)) $ _____

☐ For processing an application with a specification in a non-English language
($130.00; 37 C.F.R. §§ 1.52(d) and 1.17(k)) $ _____

☐ Processing and retention fee
($130.00; 37 C.F.R. §§ 1.53(d) and 1.21(l)) $ _____

☐ Fee for international-type search report
($40.00; 37 C.F.R. § 1.21(e)) $ _____

NOTE: 37 C.F.R. § 1.21(l) establishes a fee for processing and retaining any application that is abandoned for failing to complete the application pursuant to 37 C.F.R. § 1.53(f) and this, as well as the changes to 37 C.F.R. §§ 1.53 and 1.78(a)(1), indicate that in order to obtain the benefit of a prior U.S. application, either the basic filing fee must be paid, or the processing and retention fee of § 1.21(l) must be paid, within 1 year from notification under § 53(f).

Total fees enclosed $_____

14. Method of Payment of Fees

☐ Check in the amount of $_____

☐ Charge Account No. _____ in the amount of $_____.

A duplicate of this transmittal is attached.

NOTE: Fees should be itemized in such a manner that it is clear for which purpose the fees are paid. 37 C.F.R. § 1.22(b).

15. Authorization to Charge Additional Fees

WARNING: *If no fees are to be paid on filing, the following items should not be completed.*

WARNING: *Accurately count claims, especially multiple dependent claims, to avoid unexpected high charges, if extra claim charges are authorized.*

☐ The Commissioner is hereby authorized to charge the following additional fees by this paper and during the entire pendency of this application to Account No. _____:

- ☐ 37 C.F.R. § 1.16(a), (f) or (g) (filing fees)
- ☐ 37 C.F.R. § 1.16(b), (c) and (d) (presentation of extra claims)

NOTE: Because additional fees for excess or multiple dependent claims not paid on filing or on later presentation must only be paid or these claims cancelled by amendment prior to the expiration of the time period set for response by the PTO in any notice of fee deficiency (37 C.F.R. § 1.16(d)), it might be best not to authorize the PTO to charge additional claim fees, except possibly when dealing with amendments after final action.

- ☐ 37 C.F.R. § 1.16(e) (surcharge for filing the basic filing fee and/or declaration on a date later than the filing date of the application)
- ☐ 37 C.F.R. § 1.17(a)(1)–(5) (extension fees pursuant to § 1.136(a)).
- ☐ 37 C.F.R. § 1.17 (application processing fees)

NOTE: ". . .A written request may be submitted in an application that is an authorization to treat any concurrent or future reply, requiring a petition for an extension of time under this paragraph for its timely submission, as incorporating a petition for extension of time for the appropriate length of time. An authorization to charge all required fees, fees under § 1.17, or all required extension of time fees will be treated as a constructive petition for an extension of time in any concurrent or future reply requiring a petition for an extension of time under this paragraph for its timely submission. Submission of the fee set forth in § 1.17(a) will also be treated as a constructive petition for an extension of time in any concurrent reply requiring a petition for an extension of time under this paragraph for its timely submission." 37 C.F.R. § 1.136(a)(3).

- ☐ 37 C.F.R. § 1.18 (issue fee at or before mailing of Notice of Allowance, pursuant to 37 C.F.R. § 1.311(b))

NOTE: Where an authorization to charge the issue fee to a deposit account has been filed before the mailing of a Notice of Allowance, the issue fee will be automatically charged to the deposit account at the time of mailing the notice of allowance. 37 C.F.R. § 1.311(b).

NOTE: 37 C.F.R. § 1.28(b) requires "Notification of any change in status resulting in loss of entitlement to small entity status must be filed in the application . . . prior to paying, or at the time of paying, . . . the issue fee. . . " From the wording of 37 C.F.R. § 1.28(b), (a) notification of change of status must be made even if the fee is paid as "other than a small entity" and (b) no notification is required if the change is to another small entity.

16. Instructions as to Overpayment

NOTE: ". . . Amounts of twenty-five dollars or less will not be returned unless specifically requested within a reasonable time, nor will the payer be notified of such amounts; amounts over twenty-five dollars may be returned by check or, if requested, by credit to a deposit account." 37 C.F.R. § 1.26(a).

☐ Credit Account No. _____

☐ Refund

SIGNATURE OF PRACTITIONER

Reg. No. 32,243

David H. Jaffer

PILLSBURY MADISON & SUTRO

(type or print name of attorney)

Tel. No. (650) 233-4510

2250 Hanover Street

Palo Alto, CA 94304-1115

P.O. Address

Customer No.

☒ **Incorporation by reference of added pages**

(check the following item if the application in this transmittal claims the benefit of prior U.S. application(s) (including an international application entering the U.S. stage as a continuation, divisional or C-I-P application) and complete and attach the ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED)

☒ Plus Added Pages for New Application Transmittal Where Benefit of Prior U.S. Application(s) Claimed

Number of pages added 5

☐ Plus Added Pages for Papers Referred to in Item 4 Above

Number of pages added ______

☐ Plus added pages deleting names of inventor(s) named in prior application(s) who is/are no longer inventor(s) of the subject matter claimed in this application.

Number of pages added ______

☐ Plus "Assignment Cover Letter Accompanying New Application"

Number of pages added ______

☐ **Statement Where No Further Pages Added**

(if no further pages form a part of this Transmittal, then end this Transmittal with this page and check the following item)

☐ This transmittal ends with this page.

Practitioner's Docket No. 38559-257945 (6565-03) ***PATENT***

ADDED PAGES FOR APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED

NOTE: See 37 C.F.R. § 1.78.

17. Relate Back

WARNING: *If an application claims the benefit of the filing date of an earlier filed application under 35 U.S.C. §§ 120, 121 or 365(c), the 20-year term of that application will be based upon the filing date of the earliest U.S. application that the application makes reference to under 35 U.S.C. §§ 120, 121 or 365(c). (35 U.S.C. § 154(a)(2) does not take into account, for the determination of the patent term, any application on which priority is claimed under 35 U.S.C. §§ 119, 365(a) or 365(b).) For a c-i-p application, applicant should review whether any claim in the patent that will issue is supported by an earlier application and, if not, the applicant should consider canceling the reference to the earlier filed application. The term of a patent is not based on a claim-by-claim approach. See Notice of April 14, 1995, 60 Fed. Reg. 20,195, at 20,205.*

(complete the following, if applicable)

☐ Amend the specification by inserting, before the first line, the following sentence:

A. 35 U.S.C. § 119(e)

NOTE: "Any nonprovisional application claiming the benefit of one or more prior filed copending provisional applications must contain or be amended to contain in the first sentence of the specification following the title a reference to each such prior provisional application, identifying it as a provisional application, and including the provisional application number (consisting of series code and serial number)." 37 C.F.R. § 1.78(a)(4).

☒ "This application claims the benefit of U.S. Provisional Application(s) No(s).:

APPLICATION NO(S).:	FILING DATE
60 / 147,435	Aug. 4, 1999 "
/	"
/	"

B. 35 U.S.C. §§ 120, 121 and 365(c)

NOTE: *"Except for a continued prosecution application filed under § 1.53(d), any nonprovisional application claiming the benefit of one or more prior filed copending nonprovisional applications or international applications designating the United States of America must contain or be amended to contain in the first sentence of the specification following the title a reference to each such prior application, identifying it by application number (consisting of the series code and serial number) or international application number and international filing date and indicating the relationship of the applications. . . . Cross-references to other related applications may be made when appropriate." (See § 1.14(a)). 37 C.F.R. § 1.78(a)(2).*

☐ "This application is a

☐ continuation

☐ continuation-in-part

☐ divisional

of copending application(s)

☐ application number 0 /________________ filed on __________"

☐ International Application ________________ filed on

________________ and which designated the U.S."

NOTE: *The proper reference to a prior filed PCT application that entered the U.S. national phase is the U.S. serial number and the filing date of the PCT application that designated the U.S.*

NOTE: *(1) Where the application being transmitted adds subject matter to the International Application, then the filing can be as a continuation-in-part or (2) if it is desired to do so for other reasons then the filing can be as a continuation.*

NOTE: *The deadline for entering the national phase in the U.S. for an international application was clarified in the Notice of April 28, 1987 (1079 O.G. 32 to 46) as follows:*

"The Patent and Trademark Office considers the International application to be pending until the 22nd month from the priority date if the United States has been designated and no Demand for International Preliminary Examination has been filed prior to the expiration of the 19th month from the priority date and until the 32nd month from the priority date if a Demand for International Preliminary Examination which elected the United States of America has been filed prior to the expiration of the 19th month from the priority date, provided that a copy of the international application has been communicated to the Patent and Trademark Office within the 20 or 30 month period respectively. If a copy of the international application has not been communicated to the Patent and Trademark Office within the 20 or 30 month period respectively, the international application becomes abandoned as to the United States 20 or 30 months from the priority date respectivley. These periods have been placed in the rules as paragraph (h) of § 1.494 and paragraph (i) of § 1.495. A continuing application under 35 U.S.C. 365(c) and 120 may be filed anytime during the pendency of the international application."

☐ "The nonprovisional application designated above, namely application _____ / ________________, filed ________, claims the benefit of U.S. Provisional Application(s) No(s).:

APPLICATION NO(S).:	**FILING DATE**
_____ /________________	__________"
_____ /________________	__________"
_____ /________________	__________"

☐ Where more than one reference is made above, please combine all references into one sentence.

18. Relate Back—35 U.S.C. § 119 Priority Claim for Prior Application

The prior U.S. application(s), including any prior International Application designating the U.S., identified above in item 17B, in turn itself claim(s) foreign priority(ies) as follows:

Country	Appln. no.	Filed on

The certified copy(ies) has (have)

☐ been filed on _____, in prior application 0 /_____, which was filed on _____.

☐ is (are) attached.

WARNING: *The certified copy of the priority application that may have been communicated to the PTO by the International Bureau may not be relied on without any need to file a certified copy of the priority application **in the continuing application.** This is so because the certified copy of the priority application communicated by the International Bureau is placed in a folder and is not assigned a U.S. serial number unless the national stage is entered. Such folders are disposed of if the national stage is not entered. Therefore, such certified copies may not be available if needed later in the prosecution of a continuing application. An alternative would be to physically remove the priority documents from the folders and transfer them to the continuing application. The resources required to request transfer, retrieve the folders, make suitable record notations, transfer the certified copies, enter and make a record of such copies in the Continuing Application are substantial. Accordingly, the priority documents in folders of international applications that have not entered the national stage may not be relied on. Notice of April 28, 1987 (1079 O.G. 32 to 46).*

19. Maintenance of Copendency of Prior Application

NOTE: The PTO finds it useful if a copy of the petition filed in the prior application extending the term for response is filed with the papers constituting the filing of the continuation application. Notice of November 5, 1985 (1060 O.G. 27).

A. ☐ Extension of time in prior application

*(This item **must** be completed and the papers filed **in the prior application,** if the period set in the prior application has run.)*

☐ A petition, fee and response extends the term in the pending **prior** application until _____.

☐ A **copy** of the petition filed in prior application is attached.

B. ☐ Conditional Petition for Extension of Time in Prior Application

(complete this item, if previous item not applicable)

☐ A conditional petition for extension of time is being filed in the pending **prior** application.

☐ A **copy** of the conditional petition filed in the prior application is attached.

20. Further Inventorship Statement Where Benefit of Prior Application(s) Claimed

(complete applicable item (a), (b) and/or (c) below)

(a) ☒ This application discloses and claims only subject matter disclosed in the prior application whose particulars are set out above and the inventor(s) in this application are

☒ the same.

☐ less than those named in the prior application. It is requested that the following inventor(s) identified for the prior application be deleted:

____

(type name(s) of inventor(s) to be deleted)

(b) ☐ This application discloses and claims additional disclosure by amendment and a new declaration or oath is being filed. With respect to the prior application, the inventor(s) in this application are

☐ the same.

☐ the following additional inventor(s) have been added:

____

(type name(s) of inventor(s) to be added)

(c) The inventorship for all the claims in this application are

☒ the same.

☐ not the same. An explanation, including the ownership of the various claims at the time the last claimed invention was made

☐ is submitted.

☐ will be submitted.

21. Abandonment of Prior Application *(if applicable)*

☐ Please abandon the prior application at a time while the prior application is pending, or when the petition for extension of time or to revive in that application is granted, and when this application is granted a filing date, so as to make this application copending with said prior application.

NOTE: According to the Notice of May 13, 1983 (103, TMOG 6-7), the filing of a continuation or continuation-in-part application is a proper response with respect to a petition for extension of time or a petition to revive and should include the express abandonment of the prior application conditioned upon the granting of the petition and the granting of a filing date to the continuing application.

22. Petition for Suspension of Prosecution for the Time Necessary to File an Amendment

WARNING: *"The claims of a new application may be finally rejected in the first Office action in those situations where (A) the new application is a continuing application of, or a substitute for, an earlier application, and (B) all the claims of the new application (1) are drawn to the same invention claimed in the earlier application, and (2) would have been properly finally rejected on the grounds of art of record in the next Office action if they had been entered in the earlier application." M.P.E.P., § 706.07(b), 7th ed.*

NOTE: Where it is possible that the claims on file will give rise to a first action final for this continuation application and for some reason an amendment cannot be filed promptly (e.g., experimental data is being gathered) it may be desirable to file a petition for suspension of prosecution for the time necessary.

(check the next item, if applicable)

☐ There is provided herewith a Petition To Suspend Prosecution for the Time Necessary to File An Amendment (New Application Filed Concurrently)

23. Small Entity (37 C.F.R. § 1.28(a))

☐ Applicant has established small entity status by the filing of a statement in parent application /_____ on _____ .

☐ A copy of the statement previously filed is included.

WARNING: *See 37 C.F.R. § 1.28(a).*

WARNING: *"Small entity status must not be established when the person or persons signing the . . . statement can **unequivocally** make the required self-certification." M.P.E.P., § 509.03, 7th ed. (emphasis added).*

24. NOTIFICATION IN PARENT APPLICATION OF THIS FILING

☐ A notification of the filing of this
(check one of the following)

☐ continuation

☐ continuation-in-part

☐ divisional

is being filed in the parent application, from which this application claims priority under 35 U.S.C. § 120.

Specification

PROCESS FOR THE FORMATION OF POLYHEDRAL OLIGOMERIC SILSESQUIOXANES

BACKGROUND OF THE INVENTION

This disclosure describes methods that enable the selective manipulation of the silicon-oxygen frameworks in polyhedral oligomeric silsesquioxane (POSS) cage molecules. It is desired to selectively manipulate the frameworks of POSS compounds because they are useful as chemical species that can be further converted or incorporated into a wide variety of chemical feed-stocks useful for the preparation of catalyst supports, monomers, polymers, and as solubilized forms of silica that can be used to replace fumed and precipitated silicas or in biological applications, and for surface modification. When incorporated into a polymeric material POSS can impart new and improved thermal, mechanical and physical properties to common polymeric materials.

A variety of POSS frameworks can be prepared in synthetically useful quantities via the hydrolytic condensation of alkyl- or aryl-trichlorosilanes. In most cases, however, hydrolytic condensation reactions of trifunctional organosilicon monomers afford complex polymeric resins and POSS molecules that are unsuitable for use in polymerization or grafting reactions because they do not possess the desired type or degree of reactive functionality. In light of the fact that many structurally well-defined silsesquioxane resins $[RSiO_{1.5}]$ and POSS molecules of the homoleptic formula $[(RSiO_{1.5})_n]_{\#}$ (where R= includes but is not limited to aliphatic, aromatic, olefinic or alkoxy groups and n = 4-14) can be prepared in good to excellent yields from readily available organosilicon monomers, there are enormous incentives for developing a methodology capable of converting these POSS species into systems bearing functionalities that are more desirable for polymerization, grafting, catalysis, or compatibilization with common organic resins. Examples of such desirable functionalities include but are not limited to: silanes, silylhalides, silanols, silylamines, organohalides, alcohols, alkoxides, amines, cyanates, nitriles, olefins, epoxides, organoacids, esters, and strained olefins.

Prior art in the silsesquioxane field has taught processes for the chemical manipulation of the organic functionalities (substituents denoted by R) contained on the silicon oxygen frameworks of polyhedral oligomeric silsesquioxanes. While these methods are highly useful for varying the organic functionality (substituents) contained on POSS molecules they are not always amenable to low-cost manufacturing nor do they offer the ability to selectively cleave and or manipulate the silicon-oxygen frameworks of such compounds. Thus, these methods are of no utility for transforming the multitude of readily available and low cost silane, silicate, polysilsesquioxane (aka T-resins or T-type siloxanes) or POSS systems.

Prior art has reported that bases (e.g., NaOH, KOH, etc.) could be used to both catalyze the polymerization of POSS into lightly networked resins or to convert selected polysilsesquioxane resins into homoleptic polyhedral oligomeric silsesquioxane structures. Marsmann et al have more recently shown that a variety of bases can be used to redistribute smaller homoleptic POSS cages into larger sized homoleptic cages. While there is precedent in the literature for treatment of silsesquioxanes and POSS systems with base, the previous art does not afford the selective manipulation of silicon-oxygen frameworks and the subsequent controlled production of POSS fragments, homoleptic POSS nanostructures, heteroleptic POSS nanostructures and functionalized heteroleptic POSS nanostructures. Furthermore, the prior art does not provide methods of producing POSS systems suitable for functionalization and subsequent polymerization or grafting reactions. This oversight in the prior art is reflective of the fact that the invention of POSS-based reagents, monomers and polymer technology has only recently been developed and consequently post-dates this prior art. Hence POSS compositions and processes relevant to the types of systems desired for POSS monomer/polymer technology were not envisioned in the prior art. Additionally the prior art does not demonstrate the action of bases on silane, silicate, or silsesquioxane feedstocks suitable for producing low-cost and high purity POSS systems.

In contrast to the prior art (Brown et al. and Marsmann et al.), the processes taught here specifically enable the development of lower cost, high purity POSS systems bearing functionalities useful as derivitizable chemical reagents and feedstocks.

SUMMARY OF THE INVENTION

This invention teaches three processes that enable the manipulation and development of POSS compounds from readily available and low-cost silicon containing feedstocks. Examples of these low cost feedstocks include but are not limited to: Polysilsesquioxanes $[RSiO_{1.5}]_{\infty}$, homoleptic Polyhedral Oligomeric Silsesquioxanes (POSS) $[(RSiO1.5)n]_{\Sigma\#}$, functionalized homoleptic POSS $[(RSiO1.5)_m(RXSiO1.0)_n]_{\Sigma\#}$, heteroleptic POSS $[(RSiO1.5)_m(RSiO1.5)_n]_{\Sigma\#}$, functionalized heteroleptic POSS $[(RSiO1.5)_m(RXSiO1.0)_n]_{\Sigma\#}$, and polyhedral oligomeric silicates $[(XSiO_{1.5})_n]_{\Sigma\#}$, and POSS fragments $[(RXSiO1.5)_n]$.

DEFINITION OF FORMULA REPRESENTATIONS FOR POSS NANOSTRUCTURES:

For the purposes of explaining this invention's processes and chemical compositions the following definition for representations of nanostructural-cage formulas is made:

Polysilsesquioxanes are materials represented by the formula $[RSiO_{1.5}]_{\infty}$ where ∞ = degree of polymerization within the material and R = organic substituent (H, cyclic or linear aliphatic

or aromatic groups that may additionally contain reactive functionalities such as alcohols, esters, amines, ketones, olefins, ethers or halides). Polysilsesquioxanes may be either homoleptic or heteroleptic. Homoleptic systems contain only one type of R group while heteroleptic systems contain more than one type of R group.

POSS nanostructure compositions are represented by the formula:

$[(RSiO_{1.5})_n]_{\Sigma\#}$ for homoleptic compositions

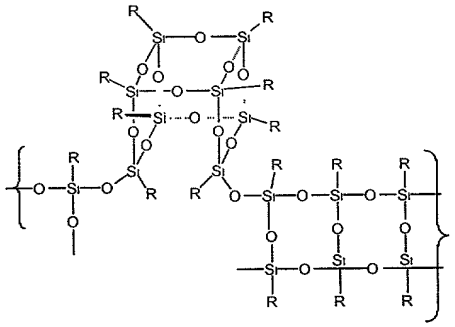
$[(RSiO_{1.5})_m(RSiO_{1.5})_n]_{\Sigma\#}$ for heteroleptic compositions

$[(RSiO_{1.5})_m(RXSiO_{1.0})_n]_{\Sigma\#}$ for functionalized heteroleptic compositions

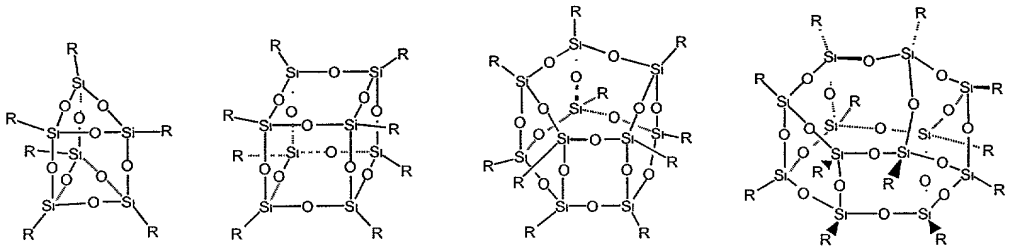
$[(XSiO_{1.5})]_{\Sigma\#}$ for homoleptic silicate compositions

In all of the above R is the same as defined above and X includes but is not limited to OH, Cl, Br, I, alkoxide (OR), acetate (OOCR), peroxide (OOR), amine (NR_2) isocyanate (NCO), and R. The symbols m and n refer to the stoichiometry of the composition. The symbol Σ indicates that the composition forms a nanostructure and the symbol # refers to the number of silicon atoms contained within the nanostructure. The value for # is usually the sum of m+n. It should be noted that Σ# is not to be confused as a multiplier for determining stoichiometry, as it merely describes the overall nanostructural characteristics of the POSS system (aka cage size).

POSS Fragments are defined as structural subcomponents that can be assembled into POSS nanostructures and are represented by formula $[(RSiO_{1.5})_m(RXSiO_{1.0})_n]$. Note the symbols Σ# are absent as these fragments are not polyhedral nanostructures.

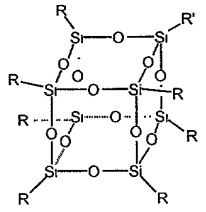


Example of Polysilsesquioxane Resins $[RSiO_{1.5}]_\infty$



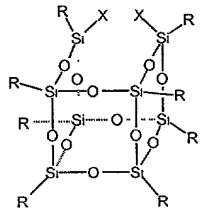
$[(RSiO_{1.5})_6]_{\Sigma 6}$ $[(RSiO_{1.5})_8]_{\Sigma 8}$ $[(RSiO_{1.5})_{10}]_{\Sigma 10}$ $[(RSiO_{1.5})_{12}]_{\Sigma 12}$

Examples of Homoleptic POSS Systems $[(RSiO_{1.5})]_{\Sigma\#}$



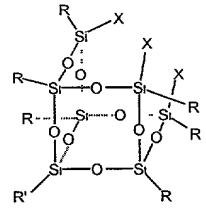
$[(RSiO_{1.5})_7(R'SiO_{1.5})_1]_{\Sigma 8}$

Example of a Heteroleptic POSS System $[(RSiO_{1.5})_m(R'SiO_{1.5})_n]_{\Sigma\#}$



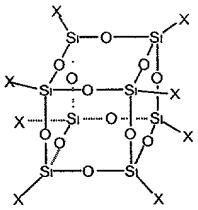
$[(RSiO_{1.5})_6(RXSiO_{1.0})_2]_{\Sigma 8}$

Example of a Functionalized Homoleptic POSS System $[(RSiO_{1.5})_m(RXSiO_{1.0})_n]_{\Sigma\#}$



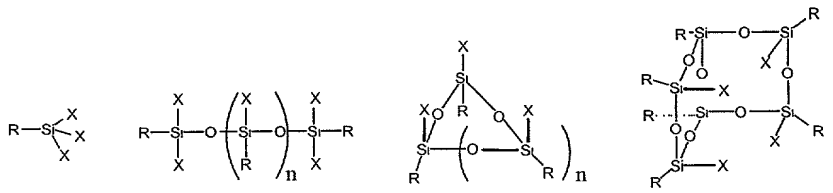
$[(RSiO_{1.5})_3(R'SiO_{1.5})_1(RXSiO_{1.0})_3]_{\Sigma 7}$

Example of a Functionalized Heteroleptic POSS System $[(RSiO_{1.5})_m(R'SiO_{1.5})_n(RXSiO_{1.0})_p]_{\Sigma\#}$



$[(XSiO_{1.5})_8]_{\Sigma 8}$

Example of a Polyhedral Oligomeric Silicate System $[(XSiO_{1.5})_n]_{\Sigma\#}$



1 2 3 4

Fragment Examples: $RSiX_3$ (1), $[(RXSiO_{0.5})_n]$ (2), $[(RXSiO_{1.0})_n]$ (3), $[(RSiO_{1.5})_m(RXSiO_{1.0})_n]$ (4)

Figure 1. Examples of Common Silsesquioxane, Silicate, POSS Nanostructures and Fragments.

GENERAL PROCESS VARIABLES APPLICABLE TO ALL PROCESSES

As is typical with chemical processes there are a number of variables that can be used to control the purity, selectivity, rate and mechanism of any process. Variables influencing the process for the conversion of polysilsesquioxanes $[RSiO_{1.5}]_\infty$ into POSS structures $[(RSiO_{1.5})_n]_{\Sigma\#}$, $[(RSiO_{1.5})_m(RSiO_{1.5})_n]_{\Sigma\#}$, $[(RSiO_{1.5})_m(RXSiO_{1.0})_n]_{\Sigma\#}$, $[(RSiO_{1.5})_m(RSiO_{1.5})_n(RXSiO_{1.0})_p]_{\Sigma\#}$ include but are not be limited to the following: chemical class of base, silicon-oxygen ring size, composition type $[RSiO_{1.5}]_\infty$ (silsesquioxane), $[(RSiO_{1.5})_n(R_2SiO)_n]_{\Sigma\#}$ (silsesquioxane-siloxane), $[(RSiO_{1.5})_m(XSiO_{1.5})_n]_{\Sigma\#}$ (silsesquioxane-silicate), effect of the organic substituents, process temperature, process solvent, process temperature, stoichiometry of base and the presence of a catalyst. Each of these variables is briefly discussed below.

Co-reagent Promoters

Specific chemical agents can be utilized to promote or enhance the effectiveness of the bases utilized in the processes. Specifically, nucleophilic base mixtures that work in combined fashion to firstly solubilize the silsesquioxane and secondly promote formation of the POSS nanostructure. Examples of such systems may include but are not limited to KOR where OR is an alkoxide, RMgX which include all common Grignard reagents, or alkalihalides such as LiI, or any of a variety of molten or fused salt media. In a similar fashion co-bases such as $[Me_3Sn][OH]$ and $[Me_4Sb][OH]$ have been shown to promote chemical transformations of POSS systems yet have not been utilized as a co-reagent in the formation of POSS cages. Alternatively, electrophilic promoters such as zinc compounds, (i.e. ZnI_2, $ZnBr_2$, $ZnCl_2$, ZnF_2, etc.) aluminum compounds, (i.e. Al_2H_6, $LiAlH_4$, AlI_3, $AlBr_3$, $AlCl_3$, AlF_3, etc.) boron compounds including (i.e. $RB(OH)_2$, BI_3, BBr_3, BCl_3, BF_3, etc.) which are known to play important roles in the solubilization and ring-opening

polymerization of cyclic silicones and in the ring-opening of polyhedral oligomeric silsesquioxanes.

Chemical Bases

The purpose of the base is to cleave the silicon-oxygen-silicon (Si-O-Si) bonds in the various silsesquioxane structures. The exact type of base, its hydration sphere, concentration, and solvent interactions all play important roles in the effectiveness of the base for cleaving the silicon-oxygen bonds. Proper understanding and control of conditions enable the selective cleavage and/or assembly of silsesquioxane, silicate, POSS, and POSS fragment systems in the desired manner. The base can also assist in the assembly of POSS fragments.

There are a wide range of bases that can be used in the processes and these include but are not limited to: hydroxide $[OH]^-$, organic alkoxides $[RO]^-$, carboxylates $[RCOO]^-$, amides $[RNH]^-$, carboxamides $[RC(O)NR]^-$, carbanions $[R]^-$ carbonate $[CO_3]^{-2}$, sulfate $[SO_4]^{-2}$, phosphate $[PO_4]^{-3}$, biphosphate $[HPO_4]^{-2}$, phosphourus ylides $[R_4P]^-$, nitrate $[NO_3]^-$, borate $[B(OH)_4]^-$, cyanate $[OCN]^-$, fluoride $[F]^-$, hypochlorite $[OCl]^-$, silicate $[SiO_4]^{-4}$, stannate $[SnO_4]^{-4}$ basic metal oxides (e.g. Al_2O_3, CaO, ZnO etc.), amines R_3N and amine oxides R_3NO, and organomtallics (e.g. RLi, R_2Zn, R_2Mg, RMgX etc.). Furthermore, the processes taught here are not limited to the above-mentioned bases; rather any reagent can be employed which produces a pH spanning the range from 7.1 to 14.

Alternatively mixtures of bases may also be utilized to carryout the process. One advantage of such an approach is that each of the bases in a given mixture can serve different functions. For example in a mixed base system one base can be used to cleave silicon-oxygen bonds or silicon-X bonds while a second base is used to assemble the POSS structure. Thus synergies can exist amongst several types of bases and these can be utilized to the advantage and refinement of these processes.

Silicon-oxygen Ring Size, Ring Type and Cage sizes

The processes discussed in this disclosure are not limited to the formation of specific sizes of POSS cages (i.e $\Sigma\#$ in $[(RSiO_{1.5})_n]_{\Sigma\#}$). Similarly the processes should not be limited to specific types of silsesquioxanes (i.e. resins, cages or fragments). They can be carried out to manufacture POSS cages containing four to eighteen or more silicon atoms in the silicon-oxygen framework. It has been noted that the silicon-oxygen ring size contained within such POSS systems does however affect the rate at which cage silicon-oxygen ring opening can occur. For example rings containing three silicon atoms and three oxygen atoms as in Formula 1 appear to open faster than the larger rings containing 4 silicon atoms and 4 oxygen atoms. The relative rate for the opening of POSS silicon-oxygen rings appears to be six member rings with three silicon atoms> eight member rings with four silicon atoms>ten member rings with five silicon atoms> twelve member rings with six silicon atoms. Selective

ring opening processes therefore can be controlled through the use of the appropriate base and knowledge of this information allows the user of these processes to control selective formation of POSS molecules.

Effect of the Organic Substituent, Process Solvents and Process Temperatures

The processes described in this disclosure are not limited to POSS systems bearing specific organic groups (defined as R) attached to the silicon atom of the silicon-oxygen ring systems. They are amenable to silsesquioxane feedstocks bearing a wide variety of organic groups (R = as previously defined) and functionalities (X= as previously defined). The organic substituent R does have a large effect on the solubility of both the final product and the starting POSS material. Therefore, it is envisioned that the different solubilities of the starting silsesquioxanes and POSS products can be used to facilitate the separation and purification of the final reaction products. We currently find no limitation of the process with respect to the type of solvent used and the processes have been carried out in common solvents including but not limited to ketones, ethers, dimethylsulfoxide, CCl_4, $CHCl_3$, CH_2Cl_2, fluorinated solvents, aromatics (halogenated and nonhalogenated), aliphatic (halogenated and nonhalogenated). Other processes can be carried out in supercritical fluids including but not limited to CO_2, H_2O, and propane. The variables of solvent type, POSS concentration, and process temperature should be utilized in the standard way to match the specific cage opening process to the equipment available. Preferred solvents for the processes are THF, MIK, and toluene. In many cases the solvent is an integral component of the process, which to enables the base to act on the specific silsesquioxane system, hence solvent effects greatly influence the degree of ionization of the base used in these processes.

Process I: Formation of POSS Systems from Polymeric Silsesquioxanes.

The current methods of preparing POSS molecules from the acid catalyzed condensation of alkyltrichlorosilanes ($RSiCl_3$) is inefficient in that it produces mixtures of POSS cage species homoleptic (POSS) $[(RSiO_{1.5})_n]_{\Sigma\#}$, functionalized homoleptic POSS $[(RSiO_{1.5})_m(RXSiO_{1.0})_n]_{\Sigma\#}$, heteroleptic POSS $[(RSiO_{1.5})_m(RSiO_{1.5})_n]_{\Sigma\#}$, functionalized heteroleptic POSS $[(RSiO_{1.5})_m(RXSiO_{1.0})_n]_{\Sigma\#}$ and polymeric silsesquioxanes $[RSiO_{1.5}]_\infty$. In some cases the undesired polymeric silsesquioxanes are produced in as much as 75% yield. It is therefore advantageous to develop a process that can efficiently convert $[RSiO_{1.5}]_\infty$ into desirable POSS nanostructures or into POSS fragments $[(RXSiO_{1.5})_n]$. Such a process will serve to not only reduce the amounts of hazardous waste produced in such reactions but will also reduce the production costs for POSS systems.

The process developed utilize bases (as defined previously), in particular hydroxide bases (e.g. sodium hydroxide, potassium hydroxide, lithium hydroxide,

benzyltrimethylammonium hydroxide, tetramethyl ammonium hyrdoxide etc) to convert polymeric silsesquioxanes $[RSiO_{1.5}]_\infty$ into homoleptic (POSS) $[(RSiO_{1.5})_n]_{\Sigma\#}$, functionalized homoleptic POSS $[(RSiO_{1.5})_n(RXSiO_{1.0})_n]_{\Sigma\#}$, heteroleptic POSS $[(RSiO_{1.5})_m(R'SiO_{1.5})_n]_{\Sigma\#}$, and functionalized heteroleptic POSS $[(RSiO_{1.5})_m(R'XSiO_{1.0})_n]_{\Sigma\#}$.

In the current process polymeric silsesquioxane $[RSiO_{1.5}]_\infty$ is dissolved or suspended in a technical grade solvent such as acetone or methylisobutyl ketone, and subsequent addition of an aqueous or alcoholic solution of base is carried out with stirring. Sufficient base should be added to the reaction mixture so as to produce a basic solution (pH 7.1-14). The reaction mixture is stirred at room temperature for 3 hours followed by heating to reflux for an additional 3-12 hours. During this time the desired POSS cages generally precipitate from the reaction medium due to their insolubility in the reaction medium. This precipitation aids in the isolation of the desired products and ensures that the products (such as the functionalized POSS species) do not undergo further reaction. In some cases it is desirable to reduce the volume of solvent by distillation or by reduced pressure in order to increase product yields or to isolate soluble POSS products. The desired POSS product is collected by filtration or decantation and can be purified through exhaustive washing with water.

We have found that hydroxide $[OH]^-$ bases are highly effective at concentrations of 1-10 equivalents (the preferred range is 2-5 equivalents per silicon atom) per mole of silicon for the conversion of aliphatic and aromatic polysilsesquioxanes $[RSiO_{1.5}]_\infty$ into homoleptic (POSS) $[(RSiO_{1.5})_n]_{\Sigma\#}$, functionalized homoleptic POSS $[(RSiO_{1.5})_m(RXSiO_{1.0})_n]_{\Sigma\#}$ heteroleptic POSS $[(RSiO_{1.5})_m(RSiO_{1.5})_n]_{\Sigma\#}$, and functionalized heteroleptic POSS $[(RSiO_{1.5})_m(RXSiO_{1.0})_n$. Hydroxyl-bases are particularly effective for producing $[(RSiO_{1.5})_m(RXSiO_{1.0})_n]_{\Sigma\#}$ POSS species. We have found that milder bases such as acetate and carbonate are more effective at converting $[RSiO_{1.5}]_\infty$ systems bearing vinyl or allyl groups. It is also recognized that the use of other co-reagents may be used to promote the formation of POSS species from this process.

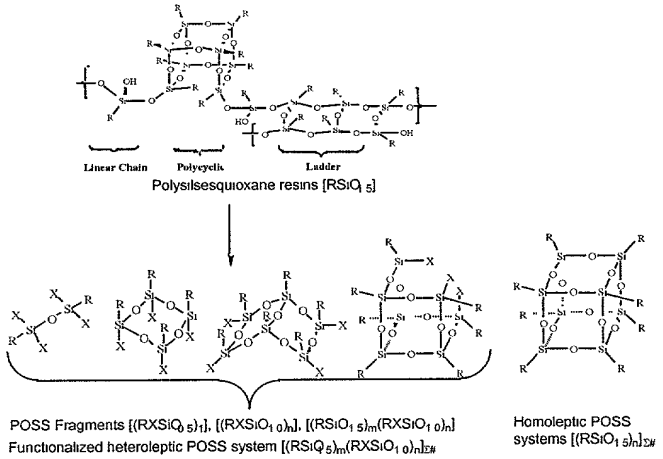


Figure 2. Illustration of Process I where polymeric silsesquioxane resins are converted into POSS fragments and nanostructures.

For the above reaction scheme the polymeric silsesquioxane resin is converted into either POSS fragments or nanostructured POSS cage species depending on the type of base and conditions employed. The conversion of polysilsesquioxanes $[RSiO_{1.5}]_\infty$ to POSS-species (homoleptic $[(RSiO_{1.5})_n]_{\Sigma\#}$, functionalized homoleptic $[(RSiO_{1.5})_m(RXSiO_{1.0})_n]_{\Sigma\#}$, heteroleptic $[(RSiO_{1.5})_m(RSiO_{1.5})_n]_{\Sigma\#}$ and functionalized heteroleptic $[(RSiO_{1.5})_m(RXSiO_{1.0})_n]_{\Sigma\#}$) or into POSS-fragments $[(RXSiO_{1.5})_n]$ can be selectively controlled through manipulation of the process variables discussed above. The process can be conducted using a polysilsesquioxane resin which may contain only one type of R group to produce homoleptic $[(RSiO_{1.5})_n]_{\Sigma\#}$ products. Alternatively the process can be carried out using polysilsesquioxane resins containing more than one type of R group or with mixtures of polysilsesquioxanes in which each contains different R groups to afford heteroleptic $[(RSiO_{1.5})_m(RSiO_{1.5})_n]_{\Sigma\#}$ products. For the above reaction scheme in which mixtures of homoleptic POSS cages (i.e. R of one POSS cage ≠ R of the second POSS cage) are substituted for the polysilsesquioxane resin the process effectively converts mixtures of homoleptically substituted POSS cages into heteroleptic POSS cages (functionalized and nonfunctionalized) that contain statistical distributions of different R groups per cage. In most cases the POSS fragments and various homo or heteroleptic nanostructured POSS species can be separated from one another through crystallization, or extractions by utilizing the differences in solubility between the reaction products and the starting silsesquioxane.

The purpose of the base in this process is to cleave silicon-oxygen bonds in the starting silsesquioxane and thereby allow for, as well as aid in the rearrangement and formation of the various POSS fragments, homoleptic and heteroleptic species. The strength of the base and the base-solvent-silsesquioxane interaction are critical factors, which enable

control over the type of products formed in these reactions. For example, increasing the basicity of the medium affords the production of POSS fragments while less basic conditions coupled with exclusion of water promote the formation of nonfunctionalized POSS species. Formation of functionalized POSS systems are favored by carrying out the process at an intermediate pH with scarce amounts of water for shorter periods of time.

Process II: Reactions between POSS Systems and Silsesquioxane/Siloxane Fragments.

The process developed utilized bases (as defined previously) to convert fragments and functionalized POSS nanostructures $[(RSiO_{1.5})_m(RXSiO_{1.0})_n]_{\Sigma\#}$ into alternate functionalized POSS nanostructures $[(RSiO_{1.5})_m(RXSiO_{1.0})_n]_{\Sigma\#}$. In the process a POSS fragment is dissolved or suspended in acetone, benzene or alcoholic solvents after which a solution of base is added with stirring. In general the reaction conditions employed in this process are milder than those used in Process I and can utilize both hydroxide and nonhydroxide bases, while the molar ratio of base relative to silicon is 1:10 (with 1:1 or 1:2 ratio being preferred).

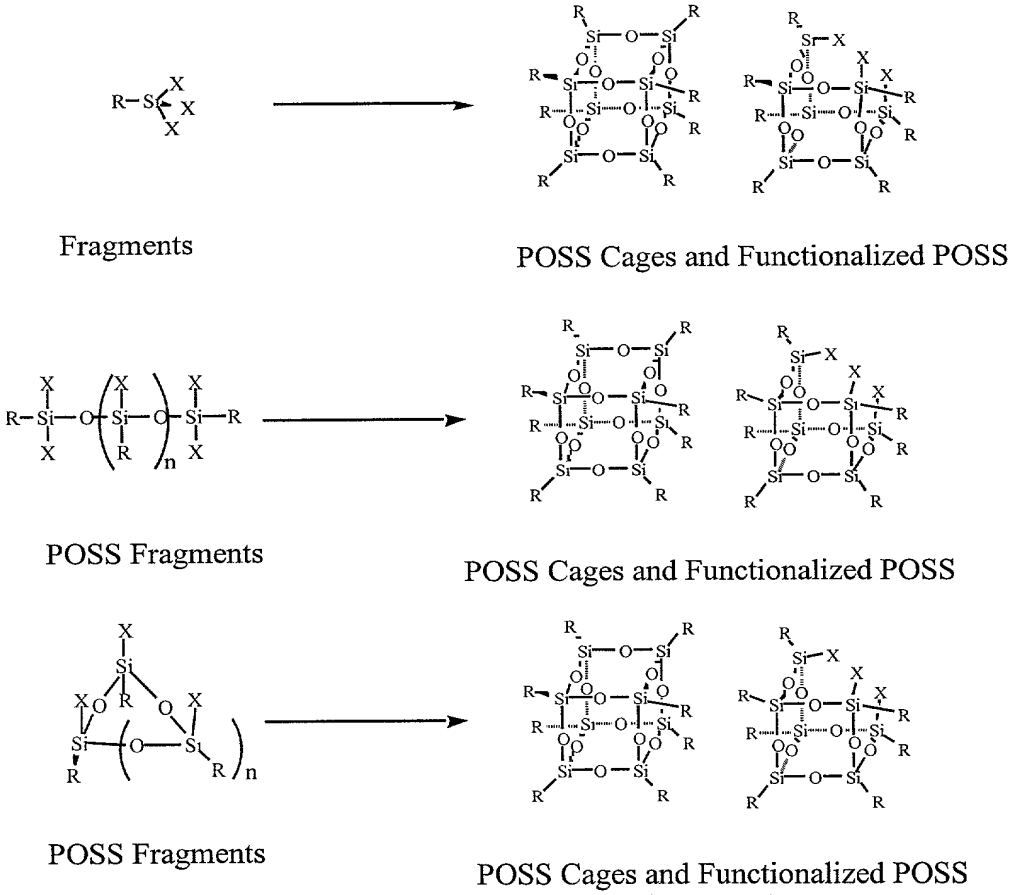


Figure 3. POSS Fragments converted into POSS cages.

The purpose of the base in this process is to cleave silicon-oxygen bonds in the starting POSS fragments. The base may also aid in the assembly of POSS structures from the fragments. A number of different bases (as defined previously) can be used to convert POSS fragments into POSS compounds. The net reaction results in the assembly of POSS fragments into POSS nanostructures, having either homoleptic or heteroleptic composition. Additionally, the resulting POSS cages may contain functional groups (i.e. $[(RSiO_{1.5})_m(RXSiO_{1.0})_n]_{\Sigma\#}$).

When mixtures of POSS fragments are utilized they are incorporated statistically into the POSS structure and their final composition is based on the stoichiometry of the starting POSS fragments. In some cases the statistical degree of substitution between these groups is governed by isomorphism resulting from the nearly identical topological shape of the R group (e.g. vinyl and ethyl). Isomorphic governance is often observed for closely related R groups (e.g. allyl and propyl etc.) however. on occasion the trend is not followed due to other factors such as rate of reaction, reagent addition, or solubility between the various POSS fragments and products. For example the reaction of 1 equivalent of EthylundeconoateSi(OMe)$_3$ or VinylSi(OMe)$_3$ with 7 equivalents of MeSi(OMe)$_3$ results in a molecule of formula 2 of the composition $[(ViSiO_{1.5})_1(MeSiO_{1.5})_7]_{\Sigma_8}$ or $[(EthylundeconoateSiO_{1.5})_1(MeSiO_{1.5})_7]_{\Sigma_8}$ despite the topological dissimilarity between the R groups.

In many cases the desired homo or heteroleptic nanostructured POSS species can be separated from one another via crystallization, extraction or by utilizing differences in the solubilities of the products and the starting POSS fragments.

An extension of this process is the action of base on functionalized POSS nanonostructures (i.e. $[(RSiO_{1.5})_m(RXSiO_{1.0})_n]_{\Sigma\#}$). It should be noted that these systems are chemically similar to a POSS fragments in terms of their chemical composition. They are different however in their topology and physical properties such as melting point, solubility and volatility.

Figure 4 illustrates actual reactions that use the conditions described in Process II as proof that the bases and conditions described in Process II are effective for the conversion of functionalized POSS cages (i.e. $[(RSiO_{1.5})_m(RXSiO_{1.0})_n]_{\Sigma\#}$) desired POSS structures. It should also be noted that in most cases these process results in an increase in the number of functionalities (X) on a POSS nanostructure while at the same time maintaining the original number of silicon atoms contained within the starting nanostructural framework. This can be desirable for a variety of subsequent synthetic product manipulations and derivations.

Figure 4 illustrates actual reactions that use the conditions described in Process II as proof that the bases and conditions described in Process II are effective for the conversion of functionalized POSS cages (i.e. $[(RSiO_{1.5})_m(RXSiO_{1.0})_n]_{\Sigma\#}$) desired POSS structures. It should also be noted that in most cases these process results in an increase in the number of

functionalities (X) on a POSS nanostructure while at the same time maintaining the original number of silicon atoms contained within the starting nanostructural framework. This can be desirable for a variety of subsequent synthetic product manipulations and derivations.

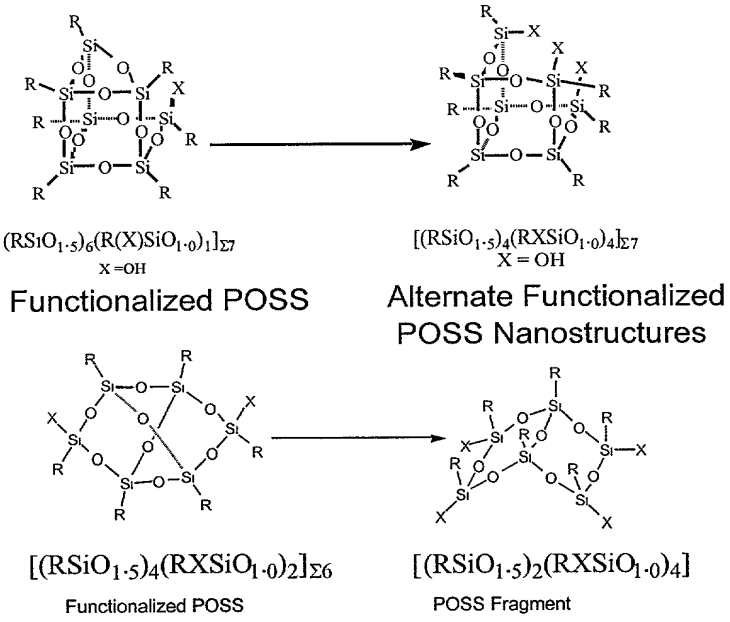
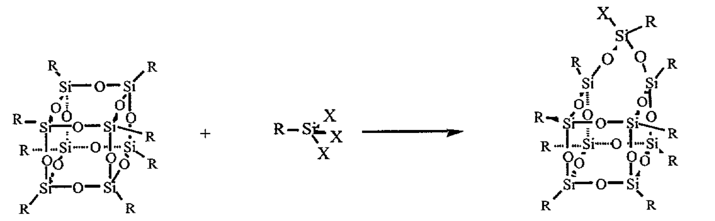


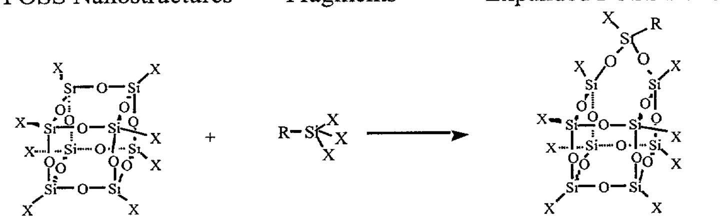
Figure 4. POSS Cages being interconverted.

The first example in Figure 4 illustrates the selectivity for the cleavage of 6 membered silicon-oxygen rings in the presence of 8 membered silicon-oxygen rings by the base, to afford the trifunctionalized POSS species. This reaction is driven by the release of greater ring strain energy from the cleavage of the 6 membered silicon-oxygen ring vs. cleavage of the 8 membered silicon-oxygen ring and is thermodynamically favorable. In the second example the energy of the twisted conformation is relieved upon cleavage to form a more open structure.

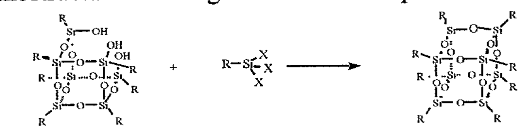
A final alternate of process II and one that is of great utility is that it can also allow for the incorporation of POSS fragments into existing POSS and POSS silicate nanostructures. This is a very important and useful aspect of this process because it allows for the expansion of both POSS and POSS silicate cage species. This is analogous to a carbon-carbon bond forming processes in organic systems. Hence this process can be utilized to prepare larger POSS nanostructures as well as POSS nanostructures having previously inaccessible sizes. Of particular importance is the use of this process to prepare nanostructures having odd as well as even numbers of silicon atoms.



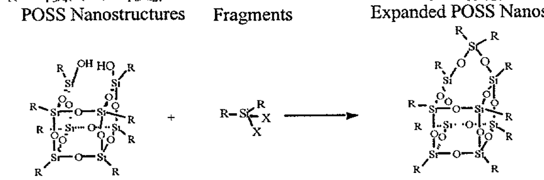
$[(RSiO_{1.5})_8]_{\Sigma 8}$ POSS Nanostructures — Fragments — $[(RSiO_{1.5})_8(RXSiO_{1.0})_1]_{\Sigma 9}$ Expanded POSS Nanostructures



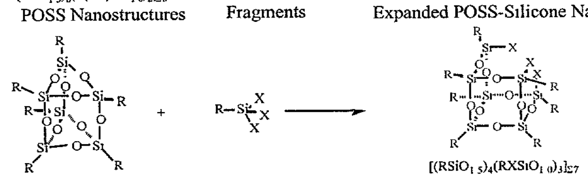
$[(XSiO_{1.5})_8]_{\Sigma 8}$ Silicate Nanostructures — Fragments — $[(XSiO_{1.5})_8(RXSiO_{1.0})_1]_{\Sigma 9}$ Expanded POSS-Silicate Nanostructures



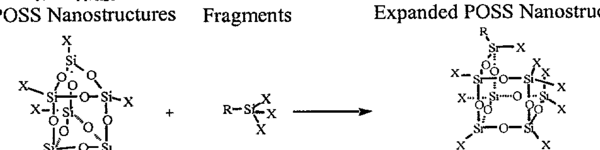
$[(RSiO_{1.5})_4(R(HO)SiO_{1.0})_3]_{\Sigma 7}$ POSS Nanostructures — Fragments — $[(RSiO_{1.5})_8]_{\Sigma 8}$ Expanded POSS Nanostructures



$(RSiO_{1.5})_6(R(HO)SiO_{1.0})_2]_{\Sigma 8}$ POSS Nanostructures — Fragments — $[(RSiO_{1.5})_8(RRSiO_{1.0})_1]_{\Sigma 9}$ Expanded POSS-Silicone Nanostructures



$[(RSiO_{1.5})_6]_{\Sigma 6}$ POSS Nanostructures — Fragments — $[(RSiO_{1.5})_4(RXSiO_{1.0})_3]_{\Sigma 7}$ Expanded POSS Nanostructures



$[(XSiO_{1.5})_6]_{\Sigma 6}$ Silicate Nanostructures — Fragments — $[(XSiO_{1.5})_4(X_2SiO_{1.0})_2(RXSiO_{1.0})_1]_{\Sigma 7}$ Expanded POSS-Silicate Nanostructures

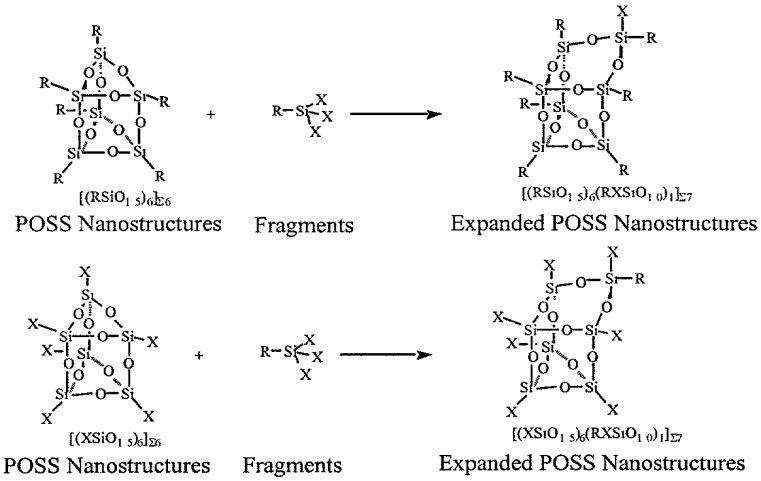


Figure 5. Silsesquioxane/siloxane fragments being inserted into POSS Cages

The net reaction in the examples shown in Figure 5 is cleavage of an Si-O-Si bond in the POSS or POSS silicate nanostructure and insertion of the POSS fragment. This reaction results in the expansion of the silicon-oxygen ring in the POSS nanostructured product. Note that the ring expansion in these reactions is in some cases favored thermodynamically through relief of ring strain in the silsesquioxane starting material. For example, the reaction of 1 equivalent of Vinyl(OMe)$_3$ with $[((c\text{-}C_6H_{11})SiO_{1.5})_6]_{\Sigma 6}$ results in POSS molecule having the composition $[((c\text{-}C_6H_{11})SiO_{1.5})_4(c\text{-}C_6H_{11})(HO)SiO_{1.0})_2(ViSiO_{1.0})_1]_{\Sigma 7}$.

Mixtures of bases may also be utilized to carryout the process. One advantage of such an approach is that the use of different types of base in combination could serve different functions. For example one base may be particularly useful for the cleavage of Si-X groups while the second base may function in the assembly of POSS fragments into POSS nanostructures. Synergistic effects between different types of base can also be expected.

Particularly important is the use of mixtures of POSS fragments (i.e. where R of one fragment ≠ R of the other fragment) or POSS fragments having more than one type of R group. Use of mixed fragments or fragments having mixed R groups affords heteroleptic POSS species $[(RSiO_{1.5})_m(RSiO_{1.5})_n]_{\Sigma\#}$ which contain more than one type of R group. In general the POSS nanostructured products formed contain a statistical mixture of R which is determined by the stoichiometry of the starting fragments. As a result, numerous isomers are possible.

Process III: Selective Opening, Functionalization and Rearrangement of POSS Nanostructures

This processes utilizes bases (as defined previously) and POSS nanostructures having homoleptic $[(RSiO_{1.5})_n]_{\Sigma\#}$ and heteroleptic $[(RSiO_{1.5})_m(RSiO_{1.5})_n]_{\Sigma\#}$ compositions. The

process allows for the conversion of low cost and easily produced unfunctionalized POSS nanostructures into more desirable functionalized POSS systems of the type $[(RSiO_{1.5})_m(RXSiO_{1.0})_n]_{\Sigma\#}$. POSS nanostuctures of the type $[(RSiO_{1.5})_m(RXSiO_{1.0})_n]_{\Sigma\#}$ can be used as stand alone chemical reagents or further derivatized to provide a diverse array of other POSS nanostructures. This process provides an entirely new synthetic route for the preparation of very important and useful incompletely condensed trisilanol reagents $[(RSiO_{1.5})_4(RXSiO_{1.0})_3]_{\Sigma7}$ in particular where X = OH.

Homoleptic POSS nanostructures $[(RSiO_{1.5})n]_{\Sigma\#}$ are readily converted into POSS nanostructures having the formula $[(RSiO_{1.5})_m(RXSiO_{1.0})_n]_{\Sigma\#}$, as well as POSS fragments having the formula $RSiX_3$, $[(RXSiO_{0.5})_n]$, $[(RXSiO_{1.0})_n]$, or $[(RSiO_{1.5})_m(RXSiO_{1.0})_n]$ through the use of bases as shown in Figure 6. Note that all possible geometric and stereochemical isomers for each product are not shown.

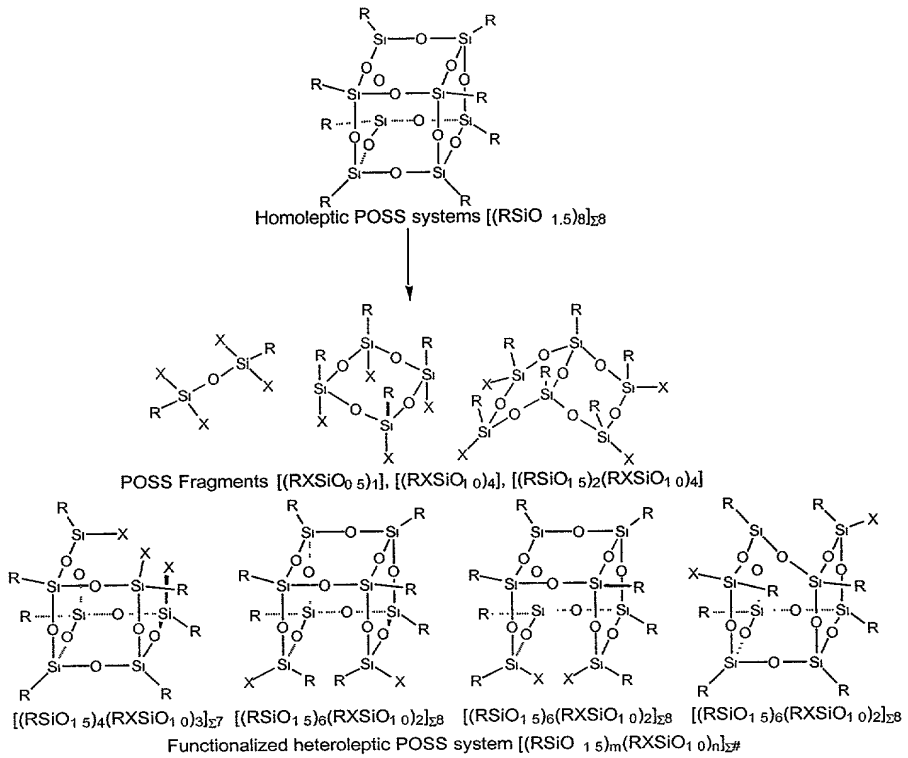


Figure 6. Illustration of Process III

Furthermore as a variation of this process it is possible to interconvert various sizes of POSS nanostructures. For example, with the proper addition of base $[(RSiO_{1\,5})_6]_{\Sigma6}$ can be either cleaved into a smaller POSS fragments (e.g. $[RSiX_3]$, $[(RXSiO_{0.5})_n]$, $[(RXSiO_{1.0})_n]$, or $[(RSiO_{1.5})_m(RXSiO_{1.0})_n]$) or functionalized into heteroleptic POSS nanostructures of the same

size (e.g. $[(RSiO_{1.5})_4(RXSiO_{1.0})_2]_{\Sigma 6}$) or larger (e.g.$[(RSiO_{1.5})_4(RXSiO_{1.0})_3]_{\Sigma 7}$) as shown in Figure 6.

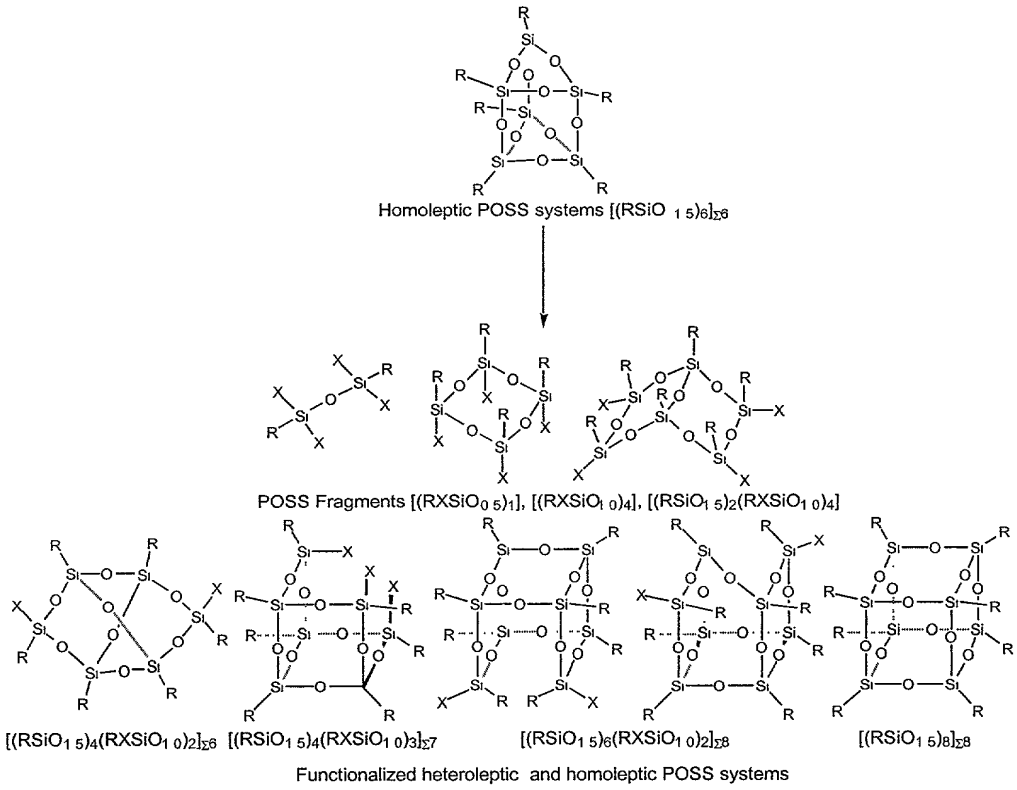


Figure 7. Illustration of Process III

As a variation of the above it is recognized that this process can utilize mixtures and distributions of POSS cages as well as polyhedral oligomeric silicate species (e.g. $[((CH_3)_3SiO)SiO_{1.5})_6]_{\Sigma 6}$, $[((CH_3)_4NO)SiO_{1.5})_6]_{\Sigma 6}$, $[((CH_3)_3SiO)SiO_{1.5})_8]_{\Sigma 8}$, $[((CH_3)_4NO)SiO_{1.5})_8]_{\Sigma 8}$. In such cases the base effectively converts cages of several sizes into functionalized and nonfunctionalized heteroleptic POSS nanostructures as shown in Figure 7. This represents an entirely new synthetic route for the preparation of the very useful incompletely condensed trisilanol reagents $[(RSiO_{1.5})_4(RXSiO_{1.0})_3]_{\Sigma 7}$ in particular where X = OH.

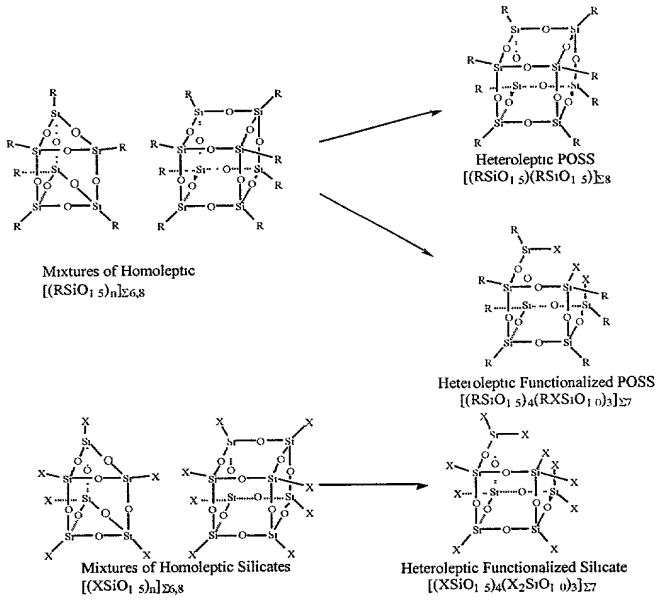


Figure 8. Illustration of the conversion of POSS and Silicate Nanostructures - Process III

A final variation of this process is the selective action of base on heteroleptic POSS nanostructures. POSS nanostructures bearing more than one type of R group per cage $[(RSiO_{1.5})_m(RSiO_{1.5})_n]_{\Sigma\#}$ are readily converted through the use of base into functionalized POSS nanostructures $[(RSiO_{1.5})_m(RXSiO_{1.0})_n]_{\Sigma\#}$. Note that all possible geometric and stereochemical isomers are not shown.

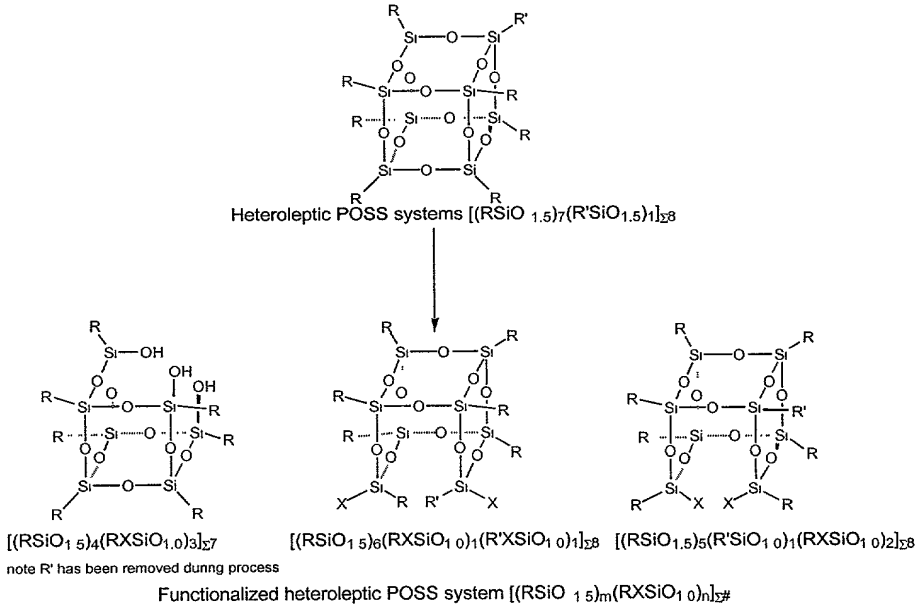


Figure 9. Illustration of the conversion of POSS Nanostructures - Process III

The action of base in the described in the preceding paragraph can also be controlled selectively so that silicon atoms can be removed entirely from the silicon oxygen framework of a polyhedral oligomeric silsesquioxane. This represents an entirely new synthetic route for the preparation of the very useful incompletely condensed trisilanol reagents such as $[(RSiO_{1.5})_4(RXSiO_{1.0})_3]_{\Sigma\#}$ where X = OH in particular. Note that not all stereochemical and geometrical isomers have been shown.

ADDITIONAL MATERIAL - SECTION B: ISOMERS OF POSS SYSTEMS

METHODS FOR CONTROLLING STEREOCHEMISTRY

Given the three dimensional, nanoscopic nature of POSS systems it is important to realize that a number of isomeric forms for any given formula may be produced by the processes taught in this work. The stereochemistry of these isomers can be controlled by the through methods taught in this patent however, in some cases geometrical isomers will still exist. A number of examples are provided to convey our acknowledgement of the presence of such isomers and that we in no way limit our claims to any one specific stereochemical or geometrical isomer.

Six isomers are possible for difunctional, incompletely condensed POSS nanostructures $[(RSiO_{1.5})_4(RXSiO_{1.0})_2]_{\Sigma_6}$ as shown in Figure 10.

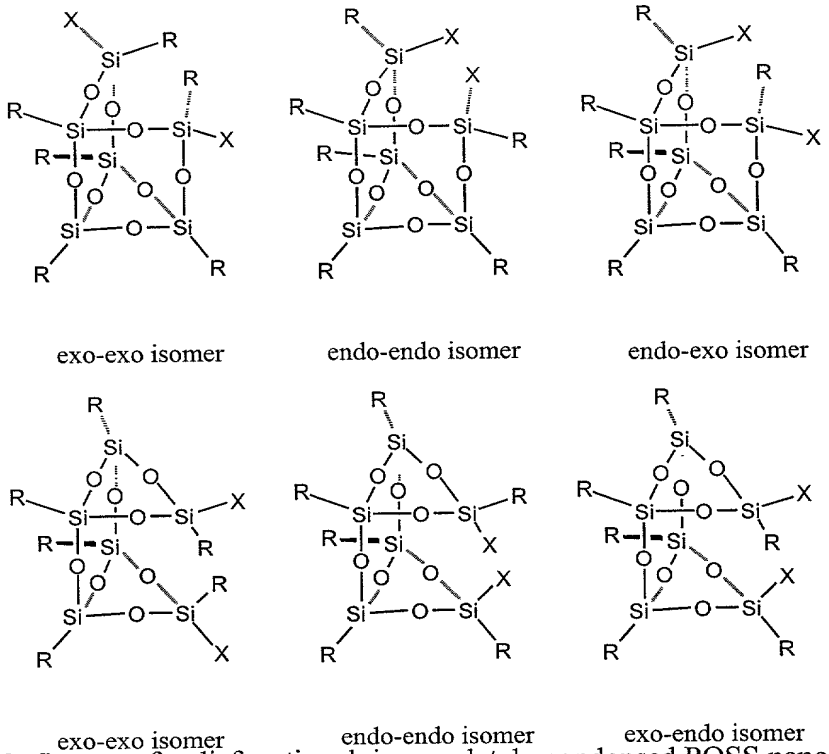


Figure 10. Isomers for disfunctional, incompletely condensed POSS nanostructures $[(RSiO_{1.5})_4(RXSiO_{1.0})_2]_{\Sigma_6}$

EXAMPLES

NMR spectra were recorded on Omega-500 (^{1}H, 500 MHz; ^{13}C, 125 MHz; ^{29}Si, 99 MHz). tetrahydrofuran, methylisobutyl ketone were distilled prior to use. All other solvents were used as purchased without purification.

Examples for Process I. The conversion of polysilsesquioxanes into POSS fragments and nanostructures.

Synthesis of $[((C_6H_5)SiO_{1.5})_8]_{\Sigma 8}$ from $[(C_6H_5)SiO_{1.5}]_\infty$ resin. Tetramethylammonium hydroxide (2.0 mL, 5.57 mmol) was added to $[(C_6H_5)SiO_{1.5}]_\infty$ resin (13.0 g, 100.6 mmol) in toluene (100 mL) at room temperature. The reaction mixture was heated to 80 °C for 12 hours, then cooled to room temperature, acidified with 1N HCl, and filtered to give 12.065 g of $[((C_6H_5)SiO_{1.5})_8]_{\Sigma 8}$ as a white solid. Product was verified by EIMS which shows a molecular ion at 1032.5 amu along with daughter ions corresponding to loss of one, two, and three phenyl groups, respectively, at 954.7, 877.4, and 800.6 amu. The above procedure can be modified for the continuous and batch production. Alternately, benzene, acetone, and methyl ethyl ketone can also be used as solvents for this reaction in place of toluene and KOH can be used instead of tetraalkylammonium bases. In addition, phenyltrimethoxysilane can be used in place of phenyl resin to prepare $[((C_6H_5)SiO_{1.5})_8]_{\Sigma 8}$.

Synthesis of $[((C_6H_5)SiO_{1.5})_{12}]_{\Sigma 12}$ from $[(C_6H_5)SiO_{1.5}]_\infty$ resin. Potassium hydroxide (46.5 g, 829 mmol) was added to $[(C_6H_5)SiO_{1.5}]_\infty$ resin (1000 g, 7740 mmol) in THF (7.8L) at roomtemperature. The reaction mixture was heated to reflux for 2 days then cooled to room temperature and filtered to give 443 g of $[((C_6H_5)SiO_{1.5})_{12}]_{\Sigma 12}$ as a microcrystalline white solid. Additional $[(C_6H_5)SiO_{1.5}]_\infty$ resin (912 g, 7059 mmol) was added to the reaction mixture and the solution was heated to reflux for 2 days followed by cooling to room temperature and filtration to give 851 g of $[((C_6H_5)SiO_{1.5})_{12}]_{\Sigma 12}$ as a microcrystalline white solid. Characterization was accomplished by EIMS which shows a molecular ion at 1548.2 amu. The above procedure can be modified for the continuous and batch production. Alternately, methylene chloride can also be used as a solvent for this reaction in place of THF and tetraalkylammonium bases can be used instead of KOH. In addition, phenyltrimethoxysilane can be used in place of $[(C_6H_5)SiO_{1.5}]_\infty$ resin to prepare $[((C_6H_5)SiO_{1.5})_{12}]_{\Sigma 12}$.

Synthesis of $[(c\text{-}C_5H_9)SiO_{1.5}]_{\Sigma 8}$ from $[(c\text{-}C_5H_9)SiO_{1.5}]_\infty$ resin. A 1.80 gram sample of resin was dissolved into 90 ml of acetone and 90 mg of NaOH was added to the reaction

mixture. The mixture was allowed to stir for 3 hours at room temperature and then was heated to reflux overnight. The solution was then cooled and filtered to obtain 1.40 g (77% yield) of pure product. The white microcrystalline powder was confirmed by X-ray diffraction and by HPLC relative to authentic sample.

Synthesis of $[((CH_2=CH)SiO_{1.5})_8]_{\Sigma 8}$ from $[(CH_2=CH)SiO_{1.5}]_\infty$ resin and $[Si_8O_{20}][NMe_4]_{\Sigma 8}$. A 0.63 g sample of resin and 2.22g of tetramethylammonium silicate salt were dissolved into 20 ml of ethanol and NMe_4OH was added to the reaction mixture until it became highly basic (pH~12). The mixture was allowed to stir for 6 days at room temperature and then was filtered to obtain 1.9 g of $[((CH_2=CH)SiO_{1.5})_8]_{\Sigma 8}$. Alternately a distribution of cages of $[((CH_2=CH)SiO_{1.5})_n]_{\Sigma n}$ where n = 8, 10, 12, 14 can be prepared in a similar manner from the reaction of $CH_2=CHSi(OCH_3)_3$ in cyclohexane with NMe_4OH followed by azeotropic distillation of water and methanol. The resulting white solid product $[(CH_2=CH)SiO_{1.5}]_{\Sigma 8\text{-}14}$ is obtained in 40% yield and is highly desirable as it is highly soluble in common solvents/reagents and melts at approximately 150°C.

Synthesis of $[((c\text{-}C_6H_9)SiO_{1.5})_4((c\text{-}C_6H_{11})SiO_{1.5})_4]_{\Sigma 8}$: In a typical reaction, a mixture of (cyclohex-3-enyl)trichlorosilane and cyclohexyltrichlorosilane were added with vigorous stirring to a solution of methanol (200 mL) and water (5 mL). The mixture was then refluxed for 2 days. Upon cooling, volatiles were removed in vacuum to afford a resin containing both cyclohexyl-Si and cyclohex-3-enyl-Si groups. Base catalyzed redistribution of this resin was accomplished by refluxing for 48 h in methyl isobutyl ketone (25 ml) with enough $C_6H_5CH_2N(CH_3)_3OH$ to produce a strongly basic solution (ca. 2 mL of 40% solution in MeOH). Evaporation of the solvent (25°C, 0.01 Torr) gave a white resinous solid, which was stirred with acetone (15 mL) and filtered to afford a mixture $[((R)SiO_{1.5})_n((R')SiO_{1.5})_n]_{\Sigma 8}$ frameworks possessing both cyclohexyl and cyclohex-3-enyl groups. Isolated yields are typically 70-80%.

Note: Excluding enantiomers, there are 22 $[((R)SiO_{1.5})_n((R')SiO_{1.5})_n]_{\Sigma 8}$ frameworks with the formula $(cyclohexyl)_n(cyclohex\text{-}3\text{-}enyl)_{8-n}Si_8O_{12}$ $(0 \le n \le 8)$. All are presumed to be present in the product mixture. The relative percentage of each compound is most dependent on the relative amounts of (cyclohex-3-enyl)trichlorosilane and cyclohexyltrichlorosilane used in the reaction, but it may also depend on other factors. The high-resolution ^{29}Si NMR spectrum (C_6D_6) of each product mixture exhibits a series of well-resolved resonances for framework Si atoms possessing cyclohexyl and cyclohexenyl groups. The chemical shifts of these resonances are constant, but the relative intensities of the resonances depend on the amount of $(cyclohex\text{-}3\text{-}enyl)SiCl_3$ and $cyclohexylSiCl_3$ used in the reaction. The product is clearly a mixture of $[((c\text{-}C_6H_{11})SiO_{1.5})_n((c\text{-}C_6H_9)SiO_{1.5})_n]_{\Sigma 8}$ frameworks. The following

chemical shift assignments (in C_6D_6) were made based on comparisons to pure, authentic samples of $[((c\text{-}C_6H_{11})SiO_{1.5})_8]_{\Sigma 8}$, $[((c\text{-}C_6H_9)SiO_{1.5})_8]_{\Sigma 8}$ and $[((c\text{-}C_6H_{11})SiO_{1.5})_n((c\text{-}C_6H_9)SiO_{1.5})_n]_{\Sigma 8}$:

Si-cyclohexenyl groups with three Si-cyclohexyl nearest neighbors: δ –67.40
Si-cyclohexenyl groups with two Si-cyclohexyl nearest neighbors: δ –67.46
Si-cyclohexenyl groups with one Si-cyclohexyl nearest neighbors: δ –67.51
Si-cyclohexenyl groups with zero Si-cyclohexyl nearest neighbors: δ –67.57
Si-cyclohexyl with three Si- cyclohexenyl groups: δ -67.91
Si-cyclohexyl with two Si- cyclohexenyl groups: δ -67.97
Si-cyclohexyl with one Si- cyclohexenyl groups: δ -68.02
Si-cyclohexyl with zero Si- cyclohexenyl groups: δ -68.08

A sample prepared by reacting equimolar amounts (0.0125 mol) of (cyclohex-3-enyl)trichlorosilane and cyclohexyltrichlorosilane as described above exhibited all 8 resonances with relative integrated intensities of approximately 4:17:17:5:4:21:22:10. A ^{13}C NMR spectrum of the same sample (in $CDCl_3$) resembles a superposition of spectra for pure $[((c\text{-}C_6H_{11})SiO_{1.5})_8]_{\Sigma 8}$ and $[((c\text{-}C_6H_9)SiO_{1.5})_8]_{\Sigma 8}$, except that resonances for ^{13}C nuclei close to the Si_8O_{12} framework are much broader due to the overlap of many resonances with slightly different chemical shifts: δ 127.45 (br m), 127.07, 27.47, 26.85, 26.63, 25.51, 25.08, 23.15, 22.64, 18.68. Analogous results were observed when $[((c\text{-}C_6H_{11})SiO_{1.5})_n((c\text{-}C_6H_9)SiO_{1.5})_n]_{\Sigma 8}$ mixtures were prepared using the following ratios of (cyclohex-3-enyl)trichlorosilane and cyclohexyltrichlorosilane:

Entry	(cyclohex-3-enyl)$SiCl_3$	cyclohexyl$SiCl_3$
1	2.7 g (12.5 mmol)	2.72 g (12.5 mmol)
2	2.7 g (12.5 mmol)	8.18 g (37.5 mmol)
3	2.7 g (12.5 mmol)	10.88 g (50 mmol)
4	6.47 g (30 mmol)	9.79 g (45 mmol)
5	1.35 g (6.25 mmol)	9.52 g (44 mmol)
6	5.82 g (27 mmol)	9.79 g (45 mmol)
7	0.68 g (3.13 mmol)	9.52 g (44 mmol)

Synthesis of $[(c\text{-}C_6H_9)SiO_{1.5}]_{\Sigma 8}$: A charge of (cyclohex-3-enyl)trichlorosilane (10.78 g, 0.05 mol) was added with vigorous stirring to a solution of methanol (200 mL) and water (5 mL). The mixture was then refluxed overnight. Upon cooling, volatiles were removed in vacuo to afford $[((c\text{-}C_6H_9)SiO_{1.5})_n]_\infty$ resin in quantitative yield. The $^{29}Si\{^1H\}$ NMR spectrum of the resin exhibits a broad featureless resonance characteristic of silsesquioxane resins and no sharp resonances attributable to discrete polyhedral silsesquioxanes (e.g., $[((R)SiO_{1.5})_n]_{\Sigma n}$ with n = 6, 8, 10, 12, 14). Base catalyzed redistribution of $[((c\text{-}C_6H_9)SiO_{1.5})_n]_\infty$ resin was accomplished by refluxing for 48 h in methyl isobutyl ketone (25 ml) with enough $C_6H_5CH_2N(CH_3)_3OH$ to produce a strongly basic solution (ca. 2 mL of 40% solution in MeOH). Evaporation of the solvent (25°C, 0.01 Torr)) gave a white resinous solid, which was stirred with acetone (15 mL) and filtered to afford $[((c\text{-}C_6H_9)SiO_{1.5})_8]_{\Sigma 8}$ in 80% yield (5.33 g) as a white, microcrystalline solid. Characterization data: ^1H NMR (500.2 MHz, $CDCl_3$, 300 K) δ 5.76 (br s, 2 H), 2.09 (br m, 4 H), 1.92 (br m, 4 H), 1.52 (br m, 1 H), 1.08 (br m, 1 H). ^{13}C NMR (125.8 MHz, $CDCl_3$, 300 K) δ 127.33, 127.08, 25.46, 25.03, 22.60, 18.60. ^{29}Si NMR (99.4 MHz, C_6D_6, 300 K) δ -67.4. The product was also characterized by a single crystal X-ray diffraction study.]

Synthesis of $[(((CH_3)_2CH)SiO_{1.5})_8]_{\Sigma 8}$: Water (1 mL) was added carefully with vigorous stirring to a solution of $(CH_3)_2CHSiCl_3$ (6.15 g, 34.8 mmol) in methanol (100 mL). The solution was then refluxed for 24 h. Upon cooling, the solvent was evaporated to afford a quantitative yield of $[i\text{-}PrSiO_{3/2}]_n$ resin as a pale yellow liquid. The $^{29}Si\{^1H\}$ NMR spectrum of the resin exhibits a broad envelope of resonances characteristic of silsesquioxane resins and indicates that very little, if any, discrete polyhedral silsesquioxanes (e.g., $[((CH_3)_2CH)SiO_{1.5}]_n$ with n = 6, 8, 10, 12, 14) are present. Base catalyzed redistribution of the $[((CH_3)_2CH)SiO_{1.5}]_n$ resin was accomplished by refluxing for 6 h in methyl isobutyl ketone (25 ml) with water (1.4 mL) and enough $C_6H_5CH_2N(CH_3)_3OH$ to produce a strongly basic solution (ca. 1 mL of 40% solution in MeOH). The crude equilibration mixture was diluted with Et_2O (200 mL), washed several times with water, dried over anhydrous $MgSO_4$ and concentrated to afford $[(((CH_3)_2CH)SiO_{1.5})_8]_{\Sigma 8}$ as a white microcrystalline powder. The yield after one equilibration is typically 15-30%, but additional $[(((CH_3)_2CH)SiO_{1.5})_8]_{\Sigma 8}$ can be obtained by base-catalyzed redistribution of $[((CH_3)_2CH)SiO_{1.5}]_\infty$ resin present in the mother liquors. The compound prepared in this fashion is identical to $[(((CH_3)_2CH)SiO_{1.5})_8]_{\Sigma 8}$ prepared via the method described by Unno (*Chemistry Letters* **1990**, 489) Characterization data: ^1H NMR (500.2 MHz, $CDCl_3$, 300 K) δ 1.036 (d, J = 6.9 Hz, 48 H, CH_3); 0.909 (sept, J

= 7.2 Hz, 8 H, CH). ^{13}C NMR (125.8 MHz, $CDCl_3$, 300 K) δ 16.78 (s, CH_3); 11.54 (s, SiCH). ^{29}Si NMR (99.4 MHz, $CDCl_3$, 300 K) δ -66.3.

Synthesis of $[((CH_3)_2CHCH_2)SiO_{1.5}]_{\Sigma 8}$: $(CH_3)_2CHCH_2SiCl_3$ (8.3 mL, 0.05 mol) was added with vigorous stirring to a mixture of CH_2Cl_2 (200 mL) and water (5 mL). The mixture was then refluxed overnight. Upon cooling, the CH_2Cl_2 layer was decanted, dried over $CaCl_2$ (5 g) and evaporated to afford $[((CH_3)_2CHCH_2)SiO_{1.5}]_\infty$ resin in quantitative yield. The $^{29}Si\{^1H\}$ NMR spectrum of the resin exhibits a broad featureless resonance characteristic of silsesquioxane resins and no sharp resonances attributable to discrete polyhedral silsesquioxanes (e.g., $[(((CH_3)_2CHCH_2)SiO_{1.5})_n]_{\Sigma n}$ with n = 6, 8, 10, 12, 14). Base catalyzed redistribution of $[((CH_3)_2CHCH_2)SiO_{1.5}]_\infty$ resin was accomplished by refluxing for 48 h in methyl isobutyl ketone (25 ml) with enough $C_6H_5CH_2N(CH_3)_3OH$ to produce a strongly basic solution (ca. 2 mL of 40% solution in MeOH). Evaporation of the solvent (25°C, 0.01 Torr)) gave a white resinous solid, which was stirred with acetone (15 mL) and filtered to afford $[(((CH_3)_2CHCH_2)SiO_{1.5})_{\Sigma 8}]$ in 30% yield (1.64 g) as a white, microcrystalline solid. Evaporation of the acetone solution gives more [i-BuSiO3/2]$_\infty$ resin, which undergoes further base catalyzed redistribution to produce more $[(((CH_3)_2CHCH_2)SiO_{1.5})_8]_{\Sigma 8}$. The combined yield of $[(((CH_3)_2CHCH_2)SiO_{1.5})_8]_{\Sigma 8}$ after three resin redistribution reactions is typically greater than 60%. Characterization data: ^1H NMR (500.2 MHz, C_6D_6, 300 K) δ 2.09 (m, 8 H, CH); 1.08 (d, J = 6.6 Hz, 48 H, CH3); 0.84 (d, J = 7.0 Hz, 16 H, CH_2). ^{13}C NMR (125.8 MHz, C_6D_6, 300 K) δ 25.6 (s, CH_3); 24.1 (s, CH); 22.7 (s, CH_2). ^{29}Si NMR (99.4 MHz, C_6D_6, 300 K) δ -67.5.

Preparation of $[((c\text{-}C_6H_{11})SiO_{1.5})_4((c\text{-}C_6H_{11})(OH)SiO_{1.0})_3]_{\Sigma 7}$ from $[(c\text{-}C_6H_{11})SiO_{1.5}]_\infty$ Resin: $[(c\text{-}C_6H_{11})SiO_{1.5}]_\infty$ resin was prepared in two steps from $C_6H_5SiCl_3$, In the first step, water was added to a toluene solution of phenyltrichlorosilane to produce $[C_6H_5SiO_{1.5}]_\infty$ resin according to the procedure reported by Brown (*J. Am. Chem. .Soc.*, (1965), *87*, 4317). This $[C_6H_5SiO_{1.5}]_\infty$ resin (1.0 g) was then dissolved in cyclohexane (50 mL) and hydrogenated to $[(c\text{-}C_6H_{11})SiO_{1.5}]_\infty$ resin in a Parr minireactor (150 °C, 220 psi, 48 h) using 10% Pd/C (1.3 g) as the catalyst. Filtration to remove the catalyst and evaporation of the solvent in vacuo afforded the $[(c\text{-}C_6H_{11})SiO_{1.5}]_\infty$ resin as a white solid. The ^1H NMR spectrum of this resin exhibits broad featureless resonances characteristic of $c\text{-}C_6H_{11}Si$ groups and no resonances attributable to C_6H_5Si groups. The $^{29}Si\{^1H\}$ NMR spectrum exhibits a broad featureless resonance characteristic of cyclohexyl silsesquioxane resins and no sharp resonances

attributable to discrete polyhedral silsesquioxanes (e.g., $[((c\text{-}C_6H_{11})SiO_{1.5})]_{\Sigma n}$ with n = 6, 8, 10, 12, 14).

Base catalyzed redistribution of $[(c\text{-}C_6H_{11})SiO_{1.5}]_\infty$ resin (0.5 g) was accomplished by refluxing in methyl isobutyl ketone (40 ml) with 35% aqueous NEt_4OH (2 mL, 5 mmol) in MIK (40 mL) for 10 h. After cooling, the solution was decanted and evaporated to dryness in vacuo to afford a brownish solid. Analysis of this solid by $^{29}Si\{^1H\}$ NMR spectroscopy and HPLC indicated the formation of $[((c\text{-}C_6H_{11})SiO_{1.5})_4((c\text{-}C_6H_{11})(OH)SiO_{1.0})_3]_{\Sigma 7}$ in 10-15% yield.

Examples for Process II: Reactions between POSS Systems and Silsesquioxane/Siloxane Fragments.

Preparation of $[((CH_3)SiO_{1.5})_7(CH_3CH_2OOC(CH_2)_{10})SiO_{1.5})_1]_{\Sigma 8}$: One equivalent of ethylundecanoate triethoxysilane and seven equivalents of methyltrimethoxy silane (1.9g) (were added dropwise to a refluxing solution of acetone (40ml) and 1 ml of water containing 0.15 equivalents, 235.6 mg) of potassium acetate. The reaction was refluxed for 3 days cooled and the white crystalline product was collected via filtration and was washed with MeOH to remove resin. The product was characterized by MS and X-ray diffraction. A similar procedure was followed for each of the following compounds:

$[((CH_3)SiO_{1.5})_6(CH_3(CH_2)_7)SiO_{1.5})_2]_{\Sigma 8}$, $[((CH_3)SiO_{1.5})_7(CH_2{=}CH)SiO_{1.5})_1]_{\Sigma 8}$,

$[((CH_3)SiO_{1.5})_4(CH_2{=}CH)SiO_{1.5})_4]_{\Sigma 8}$, $[((CH_3)SiO_{1.5})_6(CH_2{=}CH)SiO_{1.5})_2]_{\Sigma 8}$,

$[((CH_3)SiO_{1.5})_7(H_2N(CH_2)_3)SiO_{1.5})_1]_{\Sigma 8}$, $[((C_6H_5)SiO_{1.5})_7((CH_2{=}CH)SiO_{1.5})_1]_{\Sigma 8}$,

$[((CH_3)SiO_{1.5})_7(H_2N(CH_2)_3)SiO_{1.5})_1]_{\Sigma 8}$, $[((c\text{-}C_5H_9)SiO_{1.5})_7((CH_3CH_2OOC(CH_2)_{10})SiO_{1.0})_1]_{\Sigma 8}$,

$[((c\text{-}C_5H_9)SiO_{1.5})_7((CH_2{=}CH)SiO_{1.0})_1]_{\Sigma 8}$.

Preparation of $[((c\text{-}C_6H_{11})SiO_{1.5})]_{\Sigma 6,8}$: A 1.23g charge of $[((c\text{-}C_6H_{11})(OH)_2SiOSi(OH)_2(c\text{-}C_6H_{11})]$ was added to ethanol (50ml) followed by the addition of 5meq of $KHCO_3$. The reaction mixture was then allowed to react during reflux for 3 hours then the mixture was made basic through the addition of Bu_4NOH and refluxed for 2 days. The reaction was then allowed to cool and neutralized with the addition of acetic acid and the volatiles removed under reduced pressure. The residue was washed with MeOH repeatedly and dried. Yield of product 93%. The product was characterized by MS and X-ray diffraction.

Preparation of $[((c\text{-}C_6H_{11})SiO_{1.5})_8]_{\Sigma 8}$: Mixtures of $[((c\text{-}C_6H_{11})SiO_{1.5})_6]_{\Sigma 6}[((c\text{-}C_6H_{11})SiO_{1.5})_6((c\text{-}C_6H_{11})(OH)SiO_{1.0})_2]_{\Sigma 8}$ and $[((c\text{-}C_6H_{11})SiO_{1.5})_4((c\text{-}C_6H_{11})(OH)SiO_{1.0})_3]_{\Sigma 7}$ dissolved in methylisobutylketone and reacted with 20% aq. Et_4NOH under reflux for 4 days

produce nearly $[((c\text{-}C_6H_{11})SiO_{1.5})_8]_{\Sigma 8}$. Authenticity of product was verified relative to authentic sample.

Preparation of $[((CH_3)SiO_{1.5})]_{\Sigma 8}$: A 1.22kg (7.5 mole) charge of $(CH_3Si(OCH_3)_3$ was added to acetone (8 l) followed by the addition of 2.37 equivalents of Me_4NOH and 405 g of water. The reaction mixture was then allowed to react during reflux for 24 hours and the product was then collected by filtration. The product was washed repeatedly with MeOH and dried. Yield 466.2 g of product 93%. The product was characterized by MS and X-ray diffraction. A similar procedure can be used to prepare $[(CH_2{=}CH)SiO_{1.5})_8]_{\Sigma 8}$, $[(c\text{-}C_6H_{11})SiO_{1.5})_8]_{\Sigma 8}$. Modification of this procedure will afford continuous and batch-scale production.

Preparation of $[(CH_3CH_2)SiO_{1.5})_8]_{\Sigma 8}$: A similar procedure to that above for $[((CH_3)SiO_{1.5})_8]_{\Sigma 8}$ was followed in acetone to produce a $[(CH_3CH_2)SiO_{1.5})]_\infty$ resin which is then taken up in THF using KOH to produce $[(CH_3CH_2)SiO_{1.5})_8]_{\Sigma 8}$: ^1H NMR (500 MHz, $CDCl_3$): δ(ppm) 0.602 (q, J = 7.9 Hz, 16 H), 0.990 (t, J = 7.9 Hz, 24 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ(ppm) 4.06, 6.50; ^{29}Si NMR (99.4 MHz, $CDCl_3$): δ(ppm) -65.42. Modification of this procedure will afford continuous and batch-scale production.

Preparation of $[((CH_3)_2CH_2CHCH_3CH_2)SiO_{1.5})_n]_{\Sigma n}$ n = 8, 10. A similar procedure to that above for $[((CH_3)SiO_{1.5})_8]_{\Sigma 8}$ was followed using KOH to produce $[((CH_3)_2CH_2CHCH_3CH_2)SiO_{1.5})_n]_{\Sigma n}$ n = 8, 10 in quantitative yield. ^1H NMR (500 MHz, $CDCl_3$): δ(ppm) 0.563 (dd, J = 8.2, 15.1 Hz, 1 H), 0.750 (dd, J = 5.6, 15.1 Hz, 1 H), 0.902 (s, 9 H), 1.003 (d, J = 6.6 Hz, 3 H), 1.125 (dd, J = 6.4, 13.9 Hz, 1 H), 1.325 (br d, J = 13.9 Hz, 1 H), 1.826 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ(ppm) 23.72, 24.57, 25.06, 25.31, 25.71, 25.75, 25.78, 26.98, 29.52, 30.22, 30.28, 31.22, 53.99, 54.02, 54.33; ^{29}Si NMR (99.4 MHz, $CDCl_3$): δ(ppm) -69.93, -67.75 $[((CH_3)_2CH_2CHCH_3CH_2)SiO_{1.5})_{12}]_{\Sigma 12}$, -67.95 $[((CH_3)_2CH_2CHCH_3CH_2)SiO_{1.5})_{10}]_{\Sigma 10}$, -66.95 $[((CH_3)_2CH_2CHCH_3CH_2)SiO_{1.5})_8]_{\Sigma 8}$. EIMS: m/e 1039 (17%, M^+ $[((CH_3)_2CH_2CHCH_3CH_2)SiO_{1.5})_{10}]_{\Sigma 10}$), 1207 (100%, M^+ $[((CH_3)_2CH_2CHCH_3CH_2)SiO_{1.5})_8]_{\Sigma 8}$. Modification of this procedure will afford continuous and batch-scale production.

Preparation of $[(CF_3CH_2CH_2SiO_{1.5})_8]_{\Sigma 8}$. A similar procedure to that above for $[((CH_3)SiO_{1.5})_8]_{\Sigma 8}$ was followed using KOH and methanol as a solvent to produce the following mixture of products $[(CF_3CH_2CH_2SiO_{1.5})_8]_{\Sigma 12}$ 97.5%, $[(CF_3CH_2CH_2SiO_{1.5})_8]_{\Sigma 10}$

2.5% ^{1}H NMR (300 MHz, THF-d_8): δ(ppm) 0.978 (m, CH_2), 2.234 (m, CF_3CH_2); ^{13}C NMR (75.5 MHz, THF-d_8): δ(ppm) 4.99 (s, CH_2), 5.42 (s, CH_2), 28.14 (q, J = 30.5 Hz, CF_3CH_2), 28.32 (q, J = 30.5 Hz, CF_3CH_2), 128.43 (q, J = 276 Hz, CF_3), 128.47 (q, J = 276 Hz, CF_3); ^{29}Si NMR (59.6 MHz, THF-d_8): δ(ppm) -68.38 (T_{12}), -65.84 (T_{10}), -65.59 (T_{12}); ^{19}F {^{1}H} NMR (376.5 MHz, THF-d_8) δ(ppm) -71.67, -71.66. EIMS: m/e 1715 (100%, $M^+ - H_4CF_3$).

Preparation of $[(CH_3(CH_2)_{16}CH_2SiO_{1.5})_n]_{\Sigma n}$ where n = 8,10,12. A similar procedure to that above for $[((CH_3)SiO_{1.5})_8]_{\Sigma 8}$ was followed to produce the following mixture of products ^{1}H NMR (500 MHz, $CDCl_3$): δ(ppm) 0.604 (m, 2 H), 0.901 (t, J = 7.0 Hz, 3 H), 1.280 - 1.405 (m, 32 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ(ppm) 12.02, 14.15, 22.79, 22.89, 29.49, 29.75, 29.79, 29.85, 29.90, 32.05, 32.76; ^{29}Si NMR (99.4 MHz, $CDCl_3$): δ(ppm) -70.48, -68.04 $[(CH_3(CH_2)_{16}CH_2SiO_{1.5})_{12}]_{\Sigma 12}$, -68.22 $[(CH_3(CH_2)_{16}CH_2SiO_{1.5})_{10}]_{\Sigma 10}$, -66.31 $[(CH_3(CH_2)_{16}CH_2SiO_{1.5})_8]_{\Sigma 8}$.

Preparation of $[((CH_3)_2CHCH_2)SiO_{1.5})_4((CH_3)_2CHCH_2)(OH)SiO_{1.0})_3]_{\Sigma 7}$ from $(CH_3)_2CHCH_2Si(OCH_3)_3$: Isobutyltrimethoxysilane (93.3 g, 523.3 mmol) was added dropwise to LiOH•H_2O (10.0 g, 238.3 mmol) and water (8.0 mL, 444 mmol) in 88/12 acetone/methanol (500 mL) at reflux. The reaction mixture was heated at reflux the was acidified by quenching it into 1N HCl(aq) (500 mL) and stirring for 2h. The resulting solid was filtered and washed with CH_3CN (2 x 175 mL) and air dried. The product $[((CH_3)_2CHCH_2)SiO_{1.5})_4((CH_3)_2CHCH_2)(OH)SiO_{1.0})_3]_{\Sigma 7}$ was isolated in 94% yield at 98.8% purity. Note that the above procedure can be adapted to both continuous and batch production methods.

Preparation of $[(CH_3CH_2)SiO_{1.5})_4(CH_3CH_2)(OH)SiO_{1.0})_3]_{\Sigma 7}$: A similar procedure to that above for $[((CH_3)_2CHCH_2)SiO_{1.5})_4((CH_3)_2CHCH_2)(OH)SiO_{1.5})_3]_{\Sigma 7}$ was followed using acetone and LiOH to produce $[(CH_3CH_2)SiO_{1.5})_4(CH_3CH_2)(OH)SiO_{1.0})_3]_{\Sigma 7}$ as white crystalline solid in 40-80% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ(ppm) 0.582 (q, J = 7.9 Hz, 6 H), 0.590 (q, J = 7.9 Hz, 2 H), 0.598 (q, J = 7.9 Hz, 6 H), 0.974 (t, J = 7.9 Hz, 3 H), 0.974 (t, J = 7.9 Hz, 9 H), 0.982 (t, J = 7.9 Hz, 9H), 6.244 (br, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ(ppm) 3.98 (1), 4.04 (3), 4.50 (3), 6.42 (3), 6.46 (4); ^{29}Si NMR (99.4 MHz, $CDCl_3$): δ(ppm) -65.85 (3), -64.83 (1), -56.36 (3). MS (electrospray): m/e 617 (70%, $[M+Na]^+$), 595 (100%, $[M+H]^+$). Modification of this procedure will afford continuous and batch-scale production.

Preparation of $[((CH_3)SiO_{1.5})_7(CH_3CH_2OOC(CH_2)_{10})SiO_{1.5})_1]_{\Sigma 8}$: One equivalent of Triethoxyethylundecanoate and seven equivalents of methyltrimethoxy silane (1.9g) (were

added dropwise to a refluxing solution of acetone (40ml) and 1 ml of water containing 0.15 equivalents, 235.6 mg) of potassium acetate. The reaction was refluxed for 3 days cooled and the white crystalline product was collected via filtration and was washed with MeOH to remove resin. The product was characterized by MS and X-ray diffraction.

Preparation of $[((c\text{-}C_6H_{11})SiO_{1.5})_4((c\text{-}C_6H_{11})(OH)SiO_{1.0})_3]_{\Sigma 7}$ from $[((c\text{-}C_6H_{11})SiO_{1.5})_6((c\text{-}C_6H_{11})(OH)SiO_{1.0})_1]_{\Sigma 7}$: 35% aqueous NEt_4OH (20 μL, 0.05 mmol) is added to a THF (0.5 mL) solution of $[((c\text{-}C_6H_{11})SiO_{1.5})_6((c\text{-}C_6H_{11})(OH)SiO_{1.0})_1]_{\Sigma 7}$ (48 mg, 0.05 mmol) and mixed well through agitation. After 1.5 h at 25 °C, several drops of C_6D_6 were added and $^{29}Si\{^1H\}$ NMR spectrum was recorded. The spectrum matched the data for the previously reported for basic solutions of $[((c\text{-}C_6H_{11})SiO_{1.5})_4((c\text{-}C_6H_{11})(OH)SiO_{1.0})_3]_{\Sigma 7}$.

Preparation of $[((c\text{-}C_6H_{11})SiO_{1.5})_2((c\text{-}C_6H_{11})(OH)SiO_{1.0})_4]_{\Sigma 6}$ from $[((c\text{-}C_6H_{11})SiO_{1.5})_4((c\text{-}C_6H_{11})(OH)SiO_{1.0})_2]_{\Sigma 6}$: C_2-symmetry-$[((c\text{-}C_6H_{11})SiO_{1.5})_4((c\text{-}C_6H_{11})(OH)SiO_{1.0})_2]_{\Sigma 6}$ (38 mg, 0.05 mmol) was reacted with 35% aqueous NEt_4OH (20 μL, 0.05 mmol) in THF (0.5 mL) and after 30 minutes at 25 °C, several drops of C_6D_6 were added and $^{29}Si\{^1H\}$ NMR spectrum was recorded. The spectrum matched the spectrum of authentic $[((c\text{-}C_6H_{11})SiO_{1.5})_2((c\text{-}C_6H_{11})(OH)SiO_{1.0})_4]_{\Sigma 6}$ prepared by the reaction of $[((c\text{-}C_6H_{11})SiO_{1.5})_6]_{\Sigma 6}$ with aqueous NEt_4OH.

Preparation $[((c\text{-}C_6H_{11})SiO_{1.5})_4((c\text{-}C_6H_{11})(OH)SiO_{1.0})_3]_{\Sigma 7}$ from $[((c\text{-}C_6H_{11})SiO_{1.5})_6((c\text{-}C_6H_{11})(OH)SiO_{1.0})_1]_{\Sigma 7}$: A solution of $[((c\text{-}C_6H_{11})SiO_{1.5})_6((c\text{-}C_6H_{11})(OH)SiO_{1.0})_1]_{\Sigma 7}$ (0.46 mmol) and 35% aqueous NEt_4OH (0.2 mL, 0.49 mmol) was refluxed in THF (5 mL) for 5 h then neutralized with dilute aqueous HCl. Evaporation of the volatiles afforded a white solid, which was dissolved in Et_2O and dried over anhydrous $MgSO_4$. Filtration and evaporation of the solvent afforded a white microcrystalline solid in high yield. Analysis of the product mixture by ^{29}Si NMR spectroscopy indicated that the major product was $[((c\text{-}C_6H_{11})SiO_{1.5})_4((c\text{-}C_6H_{11})(OH)SiO_{1.0})_3]_{\Sigma 7}$; small amounts of $[((c\text{-}C_6H_{11})SiO_{1.5})_8]_{\Sigma 8}$ were also present.

Preparation of $[((c\text{-}C_5H_9)SiO_{1.5})_8((CH_3)_2SiO_{1.0})_1]_{\Sigma 9}$ from $[((c\text{-}C_5H_9)SiO_{1.5})_8]_{\Sigma 8}$: Reaction of $[((c\text{-}C_5H_9)SiO_{1.5})_8]_{\Sigma 8}$ (2.21 g, 2.28 mmol) and octamethyltetracyclosiloxane (1.35 g, 4.56 mmol) in 2 mL toluene with Me_4NOH (9.4 mg of 25% solution in MeOH, 0.626 mmol) is allowed for 24 h at 120 °C. The mixture is then quenched with 6 N HCl (1 mL), extracted with Et_2O (3 mL), evaporated to dryness to give a white pasty solid which contains a mixture of 70% $[((c\text{-}C_5H_9)SiO_{1.5})_8((CH_3)_2SiO_{1.0})_1]_{\Sigma 9}$,

polydimethylsiloxane, and 29% $[((c\text{-}C_5H_9)SiO_{1.5})_8]_{\Sigma 8}$. Analysis by $^{29}Si\{^1H\}$ NMR ($CDCl_3$) spectroscopy revealed $[((c\text{-}C_5H_9)SiO_{1.5})_8((CH_3)_2SiO_{1.0})_1]_{\Sigma 9}$ at (δ -65.76, -68.30, -68.34, 2:2:4).

Preparation of $[((CH_3)_2CHCH_2)SiO_{1.5})_8((5\text{-norbornene-2-ethyl})(CH_3))SiO_{1.5})_1]_{\Sigma 9}$ from $[((CH_3)_2CHCH_2)SiO_{1.5})_6((CH_3)_2CHCH_2)(OH)SiO_{1.0})_2]_{\Sigma 8}$. An Et_2O (5 mL) solution of $[((CH_3)_2CHCH_2)SiO_{1.5})_6((CH_3)_2CHCH_2)(OH)SiO_{1.0})_2]_{\Sigma 8}$ (890 mg, 1.00 mmol) was added a mixture of dichloromethyl(5-norbornene-2-ethyl)silane (endo/exo = 3/1, 282.3 mg, 1.20 mmol), Et_3N (195 μL, 1.4 mmol), and Et_2O (5 mL) at –35 °C. After addition the resulting mixture was warmed to room temperature and stirred for 20 h. The mixture was hydrolyzed and extracted with diethyl ether, washed with brine, and dried over Na_2SO_4. Evaporation of the volatiles gave $[((CH_3)_2CHCH_2)SiO_{1.5})_8((5\text{-norbornene-2-ethyl})(CH_3))SiO_{1.5})_1]_{\Sigma 9}$ (720 mg, 0.68 mmol) as a white powder in 68% yield. ^1H NMR ($CDCl_3$) δ 0.10 (s, 9H), 0.12 (s, 3H), 0.48-0.68 (m, 72H), 0.84-1.05 (m, 194H), 1.06-1.36 (m, 18H), 1.40-1.50 (m, 4H), 1.80-1.94 (m, 32H), 1.95-2.03 (m, 3H), 2.55 (br s, 1H), 2.77 (br s, 3H), 2.78-2.83 (m, 4H), 5.93 (q, ^3J = 5 Hz, ^3J = 10 Hz, 3H), 6.04 (q, ^3J = 5 Hz, ^3J = 10 Hz, 1H), 6.09-6.14 (m, 4H). ^{13}C NMR ($CDCl_3$) δ –1.11, 15.86, 16.21, 22.58, 23.20, 23.83, 23.98, 24.06, 24.18, 25.76, 25.81, 25.89, 27.71, 29.50, 32.41, 33.10, 41.89, 41.97, 42.09, 42.65, 45.10, 45.20, 46.03, 49.61, 132.35, 136.29, 136.87, 136.96. ^{29}Si NMR ($CDCl_3$) δ –69.25, –69.23, –69.21, –69.15, –67.04, –21.73, –21.63.

Preparation $[((CH_3)SiO_{1.5})_7(CH_2{=}CCH_3(O)CO(CH_2)_3)SiO_{1.5})_1]_{\Sigma 8}$: An Et_2O (80 mL) solution of Methacryloxypropyltrichlorosilane (0.69 mL, 3.31 mmol) and 1,8-bis(dimethylamino)naphthalene (2.34 g, 10.91 mmol) was added to an Et_2O (20 mL) solution of $[((CH_3)SiO_{1.5})_4((CH_3)(OH)SiO_{1.0})_3]_{\Sigma 7}$ (1.26 g, 2.54 mmol) at -35 °C. The mixture was further stirred at room temperature for 5 h and then concentrated under reduced pressure. The residue was extracted with ether. The insoluble materials were filtered. The filtrate was concentrated to give an oil-like solid. The solid was passed through a silica gel column using hexane/Et_2O (50:1) as an eluent. Evaporation of the volatiles gave $[((CH_3)SiO_{1.5})_7(CH_2{=}CCH_3(O)CO(CH_2)_3)SiO_{1.5})_1]_{\Sigma 8}$ (415 mg, 0.64 mmol) as a white solid in 25% yield. ^1H NMR ($CDCl_3$) δ 0.136 (s, 3H), 0.142 (s, 12H), 0.146 (s, 6H), 0.64-0.72 (m, 2H), 1.72-1.82 (m, 2H), 1.94 (s, 3H), 4.11 (t, J = 6.78 Hz, 3H), 5.54 (t, J = 1.58 Hz, 1H), 6.10 (br s, 1H). ^{13}C NMR ($CDCl_3$) δ –4.56, –

4.48, 8.24, 18.31, 22.19, 66.46, 125.16, 136.53, 167.46. ^{29}Si NMR ($CDCl_3$) δ -67.71, -66.00,-65.69. Calcd for $C_{14}H_{32}O_{14}Si_8$: C, 25.91; H, 4.97. Found: C, 25.69; H, 4.99.

Preparation of $[((CH_3C_6H_4SiO_{1.5})_8((CH_2=CCH_3)(O)CO(CH_2)_3)(H_3C)SiO_{1.0})_1]_{\Sigma 9}$: An Et_2O (20 mL) solution of a mixture of $[((CH_3C_6H_5)SiO_{1.5})_6((CH_3C_6H_5)(OH)SiO_{1.0})_2]_{\Sigma 8}$/$[((CH_3C_6H_5)SiO_{1.5})_8]_{\Sigma 8}$ (581.9 mg, 4/1, 0.40 mmol) was added a mixture of dichloromethacryloxypropylmethylsilane (108.8 μL, 0.50 mmol), Et_3N (139.4 μL, 1.00 mmol), and Et_2O (3 mL) at room temperature and stirred for 20 h, was then hydrolyzed, and extracted with diethyl ether. The extract was washed with brine, dried over Na_2SO_4 and after evaporation of the volatiles gave $[((CH_3C_6H_4SiO_{1.5})_8((CH_2=CCH_3)(O)CO(CH_2)_3)(H_3C)SiO_{1.0})_1]_{\Sigma 9}$ (475.5 mg, 0.36 mmol) as a white solid in 89% yield. ^{1}H NMR ($CDCl_3$) δ 0.43 (s, 3H), 0.85-0.90 (m, 2H), 1.87-1.95 (m, 2H), 1.95 (s, 3H), 2.42 (s, 6H), 2.43 (s, 12H), 2.44 (s, 6H), 4.16 (t, ^3J = 6.8 Hz, 2H), 5.56 (br s, 1H), 6.11 (br s, 1H), 7.19-7.29 (m, 18H), 7.59-7.68 (m, 10H), 7.71-7.79 (m, 4H). ^{13}C NMR ($CDCl_3$) δ -0.92, 12.87, 18.24, 21.57, 22.12, 127.14, 127.38, 127.43, 128.49, 128.55, 128.58, 128.64,133.94, 134.16, 134.19, 134.25, 140.23, 140.39, 140.59, 167.37. ^{29}Si NMR ($CDCl_3$) δ -78.72, -78.51,-76.98, -18.75.

Preparation of $[((CH_3C_6H_4SiO_{1.5})_7((CH=CH_2)(CH_3)_2SiO_{1.0})_3]_{\Sigma 7}$: A THF (15 mL) solution of $[((CH_3C_6H_5)SiO_{1.5})_8]_{\Sigma 8}$ (572.9 mg, 0.50 mmol) was added an aqueous solution of Et_4NOH (35%, 226.2 μL, 0.55 mmol) at room temperature. After addition the resulting mixture was stirred at the same temperature for 6 h. The mixture was neutralized with 1N HCl solution and extracted with diethyl ether. The organic layer was washed with brine, dried over $MgSO_4$ and volatiles evaporated to give $[((CH_3C_6H_5)SiO_{1.5})_4((CH_3C_6H_5)(OH)SiO_{1.0})_3]_{\Sigma 7}$. The $[((CH_3C_6H_5)SiO_{1.5})_4((CH_3C_6H_5)(OH)SiO_{1.0})_3]_{\Sigma 7}$ was dissolved in an Et_2O (30 mL) and a mixture of chlorodimethylvinylsilane (505 μL, 3.66 mmol), Et_3N (595 μL, 4.27 mmol), and Et_2O (3 mL) was added at room temperature and stirred for 7 h. The mixture was hydrolyzed and extracted with diethyl ether washed with brine, dried over $MgSO_4$, and evaporated to give a solid. Recrystallization of the solid from hexane afforded colorless crystals of $[((CH_3C_6H_4SiO_{1.5})_4((CH_3C_6H_5)(OSi(CH_3)_2(CH=CH_2))SiO_{1.0})_3]_{\Sigma 7}$ (230 mg, 0.18 mmol) in 36% yield. ^{1}H NMR ($CDCl_3$) δ 0.38 (s, 18H), 2.33 (s, 9H), 2.34 (s,

9H), 2.39 (s, 3H), 5.90 (dd, ^2J = 20.4 Hz, ^3J = 3.8 Hz, 3H), 6.03 (dd, ^3J = 14.9 Hz, ^3J = 3.8 Hz, 3H), 6.28 (dd, ^2J = 20.4 Hz, ^3J = 3.8 Hz, 3H), 7.01 (d, ^3J = 7.7 Hz, 12H), 7.19 (d, ^3J = 7.7 Hz, 2H), 7.27 (d, ^3J = 7.7 Hz, 6H), 7.41 (d, ^3J = 7.7 Hz, 6H), 7.53 (d, ^3J = 7.7 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 0.42, 21.51, 21.54,, 21.60, 127.51, 127.97, 128.14, 128.26, 128.55, 129.51,132.26, 134.06, 134.11, 134.17, 138.78, 139.65, 139.77, 140.37. ^{29}Si NMR ($CDCl_3$) δ -77.81, -77.29, -77.15, -0.50.

Preparation $[(((CH_3)_3SiO)SiO_{1.5})_6]_{\Sigma 6}$ from $[(((CH_3CH_2)_4NO)SiO_{1.5})_6]_{\Sigma 6}$: To a solution of trimethylchlorosilane (140.0 mL, 1.10 mol), heptane (500 mL), and N,N-dimethylformamide (200 mL) was added a powder of $[(((CH_3CH_2)_4NO)SiO_{1.5})_6]_{\Sigma 6}$ (11.9 g, 10.0 mmol) over a period of ca. 30 min at 0 °C. After addition of all the $[(((CH_3CH_2)_4NO)SiO_{1.5})_6]_{\Sigma 6}$ the mixture was stirred for an additional 30 min then allowed to warm to room temperature overnight. An ice-water (1 L) was added and the mixture stirred for 30 min. The organic layer was washed with water until neutral, dried over $MgSO_4$, and concentrated. To the residue was added a methanol and the soluble part was removed by filtration to leave a pure $[(((CH_3)_3SiO)SiO_{1.5})_6]_{\Sigma 6}$ (4.1 g, 4.84 mmol) as a white solid in 48% yield: ^{1}H NMR ($CDCl_3$) δ 0.17 (s, 54H). ^{13}C NMR ($CDCl_3$) δ 1.18. ^{29}Si NMR ($CDCl_3$) δ 14.27, –99.31.

Preparation of $[(((CH_3)_3SiO)SiO_{1.5})_6((CH_2{=}CH)(CH_3)_2SiO_{1.0})_4]_{\Sigma 6}$: To an Et_2O (5 mL) solution of vinyldimethylchlorosilane (121.5 μL, 0.88 mmol) and NEt_3 (139.4 μL, 1.00 mmol) was added an Et_2O solution of $[(((CH_3)_3SiO)SiO_{1.5})_2(((CH_3)_3SiO)(OH)SiO_{1.0})_4]_{\Sigma 6}$ (174.7 mg, 0.20 mmol) at room temperature. The mixture was stirred at room temperature for 4h and then concentrated under reduced pressure. The residue was extracted with hexane. The insoluble materials were filtered. The filtrate was concentrated to give a spectroscopic pure $[(((CH_3)_3SiO)SiO_{1.5})_6((CH_2{=}CH)(CH_3)_2SiO_{1.0})_4]_{\Sigma 6}$ (225.6 mg, 0.18 mmol) as a white foam solid in 92% yield: ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 54H), 0.14 (s, 12H), 0.18(s, 12H), 5.73 (d, J = 4.0 Hz, 2H), 5.77 (d, J = 4.0 Hz, 2H), 5.91 (d, J = 4.0 Hz, 2H), 5.94 (d, J = 4.0 Hz, 2H), 6.11 (d, J = 15.0 Hz, 2H), 6.15 (d, J = 15.0 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 0.11, 1.52, 1.62, 132.00, 138.79. ^{29}Si NMR ($CDCl_3$) δ 11.24, 10.17, –1.35, –108.31, –108.70. MS (ESI): Calcd for $C_{34}H_{90}O_{17}Si_{16}Na$, 1243.2. Found: 1243.6.

Preparation of $[(((CH_3)_3SiO)SiO_{1.5})_6((C_6H_5)SiO_{1.5})_1((CH_2{=}CCH_3)(O)CO(CH_2)_3SiO_{1.5})_1]_{\Sigma 8}$ from $[(((CH_3)_3SiO)SiO_{1.5})_4((C_6H_5)(OH)SiO_{1.0})_1(((CH_3)_3SiO)(OH)SiO_{1.0})_2]_{\Sigma 7}$: An Et_2O (8 mL) solution of methacryloxypropyltrichlorosilane (340.3

μL, 1.63 mmol) and NEt_3 (748.5 μL, 5.37 mmol) was added to an Et_2O (7 mL) solution of $[(((CH_3)_3SiO)SiO_{1.5})_4((C_6H_5)(OH)SiO_{1.0})_1(((CH_3)_3SiO)(OH)SiO_{1.0})_2]_{\Sigma 7}$ (817.0 mg, 0.81 mmol) at -35 °C and the mixture was stirred at room temperature for 6 h and then concentrated under reduced pressure. The residue was extracted with hexane, insoluble materials were filtered, and the filtrate was concentrated to give an oil. The oil was purified using a silica gel column and hexane/Et_2O (50:1) as an eluent. Evaporation of the volatiles gave $[(((CH_3)_3SiO)SiO_{1.5})_6((C_6H_5)SiO_{1.5})_1((CH_2{=}CCH_3)(O)CO(CH_2)_3SiO_{1.5})_1]_{\Sigma 8}$ (210.0 mg, 0.18 mmol) as a white solid in 25% yield. ^1H NMR ($CDCl_3$) δ 0.13 (s, 18H), 0.16 (s, 18H), 0.17 (s, 9H), 0.18 (s, 9H), 0.73-0.80 (m, 2H), 1.77-1.85 (m, 2H), 1.93 (s, 3H), 4.11 (t, J = 6.62 Hz, 2H), 5.54 (t, J = 1.58 Hz, 1H), 6.09 (br s, 1H), 7.35-7.41 (m, 2H), 7.43-7.48 (m, 1H), 7.66-7.72 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 1.24, 7.95, 18.30, 22.11, 66.39, 125.22, 127.70, 130.22, 130.69, 134.08, 136.41, 167.37. ^{29}Si NMR ($CDCl_3$) δ -109.06, -108.88,-108.82, -78.86, -65.60, 12.55, 12.58, 12.59. Calcd for $C_{31}H_{70}O_{20}Si_{14}$: C, 32.21; H, 6.10. Found: C, 31.99; H, 6.35. MS (ESI) Calcd for 1177.1 $[M + Na]^+$, 1193.1 $[M + K]^+$. Found: 1177.2 $[M + Na]^+$, 100%; 1193.2 $[M+K]^+$, 10%.

Examples for Process III: Selective Opening, Functionalization and Rearrangement of POSS Nanostructures

Preparation of $[((CH_2{=}CH)SiO_{1.5})_6((CH_2{=}CH)(HO)SiO_{1.0})_2]_{\Sigma 8}$ from $[((CH_2{=}CH)SiO_{1.5})_8]_{\Sigma 8}$: An aqueous solution of NEt_4OH (33%, 2 mL, 0.25 mmol) in THF (10 mL, -35 °C) was added to a stirred solution of $[((CH_2{=}CH)SiO_{1.5})_8]_{\Sigma 8}$ (2.95 g, 4.66 mmol) in 1:1:1 THF/CH_2Cl_2/isopropanol (300 mL), which was chilled in a -35 °C (1:1 methanol/water and N_2) cold bath. After 4.3 hours the reaction was quenched with 1*M* HCl (20 mL, -35 °C) and the solution was washed with 1*M* HCl (2 x 40 mL), water (2 x 40 mL), and sat. aq. NaCl solution (40 mL). After drying over Na_2SO_4, and removal of the solvent *in vacuo* (25 °C, 0.01 Torr) a white solid (3.01 g, 99%) was isolated. The product $[((CH_2{=}CH)SiO_{1.5})_6((CH_2{=}CH)(HO)SiO_{1.0})_2]_{\Sigma 8}$ prepared by this procedure is spectroscopically pure. Additional purification can be accomplished through recrystallization from CH_2Cl_2/hexanes/acetic acid (25 °C). ^1H NMR ($CDCl_3$, 500.2 MHz, 25 °C): δ 6.12-5.74 (m, $SiCH{=}CH_2$), 5.7 (br, SiOH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.7 MHz, 25 °C): δ 137.00, 136.87, 136.81 (s, CH_2, rel. int. 1:1:2), 129.75, 129.17, 128.80 (s, SiCH, rel. int. 1:2:1).

$^{29}Si\{^1H\}$ NMR ($CDCl_3$, 99.4 MHz, 25 °C): δ -71.39 (s, SiOH), -79.25, -80.56 (s, SiCH, rel. int. 1:2). Mass Spectrum (ESI) m/z calcd for $C_{16}H_{26}O_{13}Si_8$: $[M + H]^+$ 650.96, found 651.2 (20%); $[M + Na]^+$ 672.94, found 673.1 (100%). Mass Spectrum (EI) m/z calculated for $C_{16}H_{26}O_{13}Si_8$: $[M]^+$ 649.9528, found 649.9532 (4%); $[M - C_2H_3]^+$ 622.9, found 623.2 (100%).

Preparation of $[(Boc\text{-}NHCH_2CH_2CH_2)SiO_{1.5})_6((Boc\text{-}NHCH_2CH_2CH_2)(HO)SiO_{1.0})_2]_{\Sigma 8}$ from $[(Boc\text{-}NHCH_2CH_2CH_2)SiO_{1.5})_8]_{\Sigma 8}$: A solution of $[(Boc\text{-}NHCH_2CH_2CH_2)SiO_{1.5})_8]_{\Sigma 8}$ (0.11 mmol) in 1:1:1 CH_2Cl_2/THF/isopropanol (-35 °C, 7.5 mL) and aq. NEt_4OH (35 wt%, 50 μL, 0.13 mmol) was stirred at -35 °C for 2 h. Addition of CH_3CO_2H (0.1 mL, -35 °C), extraction with a saturated aqueous NaCl solution (3 x 10 mL), drying over Na_2SO_4, and removal of the solvent *in vacuo* (25 °C, 0.001 Torr) afforded $[(Boc\text{-}NHCH_2CH_2CH_2)SiO_{1.5})_6((Boc\text{-}NHCH_2CH_2CH_2)(HO)SiO_{1.0})_2]_{\Sigma 8}$ as a colorless paste in a 63 % yield. $^{29}Si\{^1H\}$ NMR ($CDCl_3$, 99.4 MHz, 25 °C): δ -57.798, -65.674, -67.419 (s, rel. int. 1:1:2). Mass Spectrum (ESI) m/z calcd for $C_{64}H_{130}N_8O_{29}Si_8$: $[M + Na]^+$ 1721.7, found 1722.1.

Preparation of $[(Cbz\text{-}Pro\text{-}NHCH_2CH_2CH_2)SiO_{1.5})_6((Cbz\text{-}Pro\text{-}NHCH_2CH_2CH_2)(HO)SiO_{1.0})_2]_{\Sigma 8}$ from $[(Cbz\text{-}Pro\text{-}NHCH_2CH_2CH_2)SiO_{1.5})_8]_{\Sigma 8}$: A solution of $[(Cbz\text{-}Pro\text{-}NHCH_2CH_2CH_2)SiO_{1.5})_8]_8$ (0.11 mmol) in 1:1:1 CH_2Cl_2/THF/isopropanol (-35 °C, 7.5 mL) and aq. NEt_4OH (35 wt%, 50 μL, 0.13 mmol) was stirred at -35 °C for 2 h. Addition of CH_3CO_2H (0.1 mL, -35 °C), extraction with a saturated aqueous NaCl solution (3 x 10 mL), drying over Na_2SO_4, and removal of the solvent *in vacuo* (25 °C, 0.001 Torr) afforded $[(Cbz\text{-}Pro\text{-}NHCH_2CH_2CH_2)SiO_{1.5})_6((Cbz\text{-}Pro\text{-}NHCH_2CH_2CH_2)(HO)SiO_{1.0})_2]_{\Sigma 8}$ as a colorless paste in 77 % yield. $^{29}Si\{^1H\}$ NMR ($CDCl_3$, 99.4 MHz, 25 °C): δ -58.4, -65.543, -67.470 (s, rel. int. 1:1:2). Mass Spectrum (ESI) m/z calcd for $C_{128}H_{170}N_{16}O_{37}Si_8$: $[M + Na]^+$ 2772.54, found 2772.9.

Preparation of $[((MeO_2CCH_2CMe_2CH_2CH_2CH_2)SiO_{1.5})_6((MeO_2CCH_2CMe_2CH_2CH_2CH_2)(HO)SiO_{1.0})_2]_{\Sigma 8}$ from $[((MeO_2CCH_2CMe_2CH_2CH_2CH_2)SiO_{1.5})_8]_{\Sigma 8}$: A solution of $[((MeO_2CCH_2CMe_2CH_2CH_2CH_2)SiO_{1.5})_8]_{\Sigma 8}$ (0.11 mmol) in 1:1:1 CH_2Cl_2/THF/isopropanol (-35 °C, 7.5 mL) and aq. NEt_4OH (35 wt%, 50 μL, 0.13 mmol) was stirred at -35 °C for 2 h. Addition of CH_3CO_2H (0.1 mL, -35 °C), extraction with a saturated aqueous NaCl solution (3 x 10 mL), drying over Na_2SO_4, and removal of the solvent *in vacuo* (25 °C, 0.001 Torr) afforded $[((MeO_2CCH_2CMe_2CH_2CH_2CH_2)SiO_{1.5})_6((MeO_2CCH_2CMe_2CH_2CH_2CH_2)(HO)SiO_{1.0})_2]_{\Sigma 8}$ as a colorless paste in 66 % yield. $^{29}Si\{^1H\}$ NMR ($CDCl_3$, 99.4 MHz, 25 °C): δ -57.551, -64.981, -66.841 (s, rel. int. 1:1:2). Mass Spectrum (ESI) m/z calculated for $C_{64}H_{122}O_{29}Si_8$: $[M + Na]^+$ 1601.61, found 1602.0.

Preparation of $[(((CH_3)_3SiO)SiO_{1.5})_2(((CH_3)_3SiO)(OH)SiO_{1.0})_4]_{\Sigma 6}$: To a THF (4 mL) solution of $[(((CH_3)_3SiO)SiO_{1.5})_6]_{\Sigma 6}$ (169.5 mg, 0.20 mmol) was added an aqueous solution of NEt_4OH (35%, 82.3 μL, 0.20 mmol) at –40 °C. The resulting mixture was stirred between –40 to –25 °C for 40 min. The mixture was neutralized with aqueous solution of HCl (1N, 3 mL) and extracted with diethyl ether. The organic layer was washed with brine, dried over $MgSO_4$, and evaporated to give a spectroscopic pure $[(((CH_3)_3SiO)SiO_{1.5})_2(((CH_3)_3SiO)(OH)SiO_{1.0})_4]_{\Sigma 6}$ (174.7 mg, 0.20 mmol) as a white wax solid in 99% yield. ^1H NMR ($CDCl_3$) δ 0.14 (s, 54H). ^{13}C NMR ($CDCl_3$) δ 1.24, 1.28. ^{29}Si NMR ($CDCl_3$) δ 12.44, 12.19, –100.12, –109.27.

Preparation of $[(((H_3C)_3SiO)SiO_{1.5})_6(((H_3C)_3SiO)(OH)SiO_{1.0})_2(((CH_2{=}CH)(OH)SiO_{1.0})_1]_{\Sigma 7}$: The starting polyhedral oligomeric silicate $[(((H_3C)_3SiO)SiO_{1.5})_6]_{\Sigma 6}$ was prepared via a procedure analogous to that published by Harrison et al. *Main Group Metals Chemistry* (1997) vol 20, pp. 137-141. A solution of Vinyltrimethoxysilane (0.04 mL, 0.26 mmol) and aqueous NEt_4OH (0.1 mL, 0.25 mmol) was prereacted for 10 minutes and then added to a solution of $[(((H_3C)_3SiO)SiO_{1.5})_6]_{\Sigma 6}$ (198 mg, 0.23 mmol) and was stirred for 15 minutes at room temperature. The reaction was then neutralized through the addition of dilute HCl and the solvent was removed under reduced pressure. The residue was then taken up in diethylether filtered and dried over anhydrous $MgSO_4$. Filtration and evaporation of the solvent afforded a yellow oil (2.31 mg, 0.002mol) in 10.2% yield. Selected characterization data: $^{29}Si\{^1H\}$ NMR (99.3 MHz, $CDCl_3$, 25 °C) δ -99.8, -100.1, -108.0, -108.9. MS (ESI, 100% MeOH): *m/e* 977.1 ($\{M + Na]^+$.

Preparation of $[((CH_3CH_2)SiO_{1.5})_6((CH_3CH_2)(HO)SiO_{1.0})_2]_{\Sigma 8}$ from $[((CH_3CH_2)SiO_{1.5})_8]_{\Sigma 8}$: A CH_2Cl_2/*i*-PrOH/THF(10/10/10 mL) solution of $[((CH_3CH_2)SiO_{1.5})_8]_{\Sigma 8}$ (259.7 mg, 0.40 mmol) was added an aqueous solution of Et_4NOH (35%, 493.5 μL, 1.20 mmol) at -20 °C. After addition the resulting mixture was stirred at the same temperature for 7 h. The mixture was neutralized with 1N HCl solution and extracted with diethyl ether. The organic layer was washed with brine, dried over Na_2SO_4. Evaporation of the volatiles gave spectroscopically pure $[((CH_3CH_2)SiO_{1.5})_6((CH_3CH_2)(HO)SiO_{1.0})_2]_{\Sigma 8}$ (263.5 mg, 0.39 mmol) as a white solid in 99% yield. ^1H NMR ($CDCl_3$) δ 0.54-0.66 (m, 16H), 0.93-1.04 (m, 24H), 5.21 (br s, 2H). ^{13}C NMR ($CDCl_3$) δ 3.94, 4.36, 4.41, 6.42, 6.46, 6.50. ^{29}Si NMR ($CDCl_3$) δ –66.73, –64.95,–57.63. Calcd for $C_{16}H_{42}O_{13}Si_8$: C, 28.80; H, 6.35. Found: C, 28.78; H, 6.43.

Preparation of $[(((CH_3)_2CH)SiO_{1.5})_6(((CH_3)_2CH)(HO)SiO_{1.0})_2]_{\Sigma 8}$ from $[(((CH_3)_2CH)SiO_{1.5})_8]_{\Sigma 8}$: $[(((CH_3)_2CH)SiO_{1.5})_8]_{\Sigma 8}$ (302 mg, 0.397 mmol) was dissolved in 15mL of solvents' mixture (iso-propanol:CH_2Cl_2:THF = 1:1:1). The aqueous 35% solution of EtN_4OH (0.8 mL) was added to the solution of $[(((CH_3)_2CH)SiO_{1.5})_8]_{\Sigma 8}$ at -12°C. After 7 hours, the reaction mixture was decanted, extracted with Et_2O (4 x 3 mL). The extract was dried over anhydrous Na_2SO_4, then evaporated in vacuo, obtained a yellow solid which was purified by column chromatography (SiO_2, 60%CH_2Cl_2 in hexanes) to afford a spectroscopically pure powder (189 mg, 61%). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ 3.90 (br s, SiOH, 2H), 1.03 (br m's, 48H), 0.91 (br m's, 8H. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C): δ 16.91, 16.79, 16.64 (8:4:4 for CH_3), 11.91, 11.77, 11.38 (4:2:2 for CH), $^{29}Si\{^1H\}$ NMR (99 MHz, $CDCl_3$, 25 °C): δ -57.92, -65.29, -67.70 (2:2:4). IR (25 °C, KBr, cm^{-1}): 3352, 2950, 2869, 1466, 1260, 1112. MS (ESI, 100% MeOH): m/e 802.0 {$[M+Na]^+$, 100%}, 779.1 (M^+, 70%). Anal. Calculated for $C_{24}H_{57}O_{13}Si_8$ (found): C, 37.03 (36.92), H, 7.38 (7.54).

Preparation of $[((c\text{-}C_6H_9)SiO_{1.5})_4((c\text{-}C_6H_9)(OH)SiO_{1.0})_2((CH_2{=}CH)(OH)SiO_{1.0})_1]_{\Sigma 7}$: A solution of 35% aqueous NEt_4OH (0.1 mL, 0.25 mmol) was added to a solution of $[(c\text{-}C_6H_9)SiO_{1.5}]_{\Sigma 6}$ (205 mg, 0.25 mmol) and $VinylSi(OMe)_3$ in THF (2.5 mL). The solution was stirred for 1 h then neutralized with dilute aqueous HCl. Evaporation of the volatiles afforded a white resin, which was dissolved in Et_2O and dried over anhydrous $MgSO_4$. Filtration and evaporation of the solvent afforded a white solid in high mass yield. Analysis by multinuclear NMR spectroscopy and electrospray mass spectrometry indicated that the product mixture contained a ~6:1 mixture of $[((c\text{-}C_6H_9)SiO_{1.5})_2((c\text{-}C_6H_9)(OH)SiO_{1.0})_4]$ and $[((c\text{-}C_6H_9)SiO_{1.5})_4((c\text{-}C_6H_9)(OH)SiO_{1.0})_2((CH_2{=}CH)(OH)SiO_{1.0})_1]_{\Sigma 7}$. Selected characterization data: $^{29}Si\{^1H\}$ NMR (99.3 MHz, $CDCl_3$, 25 °C) δ -60.1 (s, 2 Si, Cy-Si-OH), -68.2 (s, 1 Si), -69.1 (s, 2 Si), -69.7 (s, 1 Si), -72.0 (s, 1 Si, V-Si-OH). ^1H NMR (500 MHz, $CDCl_3$, 25 °C) δ 5.90 (m, 3 H, $-CH{=}CH_2$); 1.65, 1.16 (m, 66 H, C_5H_{11}). $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6, 25 °C) δ 135.4 (s, $=CH_2$); 130.4 (s, -CH=); 27.53, 27.47, 26.82, 26.67, 26.59, 26.56 (s, CH_2); 23.81, 23.59, 23.36, 23.10 (s, CH). MS (ESI, 100% MeOH): *m/e* 917 ($[M + H]^+$, 75%); 939 ($\{M + Na]^+$, 100

Reaction of $[((c\text{-}C_6H_{11})SiO_{1.5})_6]_{\Sigma 6}$ with NEt_4OH at room temperature: A solution of $[((c\text{-}C_6H_{11})SiO_{1.5})_6]_{\Sigma 6}$ (200 mg, 0.24 mmol) and 35% aqueous NEt_4OH (0.1 mL, 0.25 mmol) in THF (2.5 mL) was stirred at 25 °C for 4 h then neutralized with dilute aqueous HCl. Evaporation of the volatiles afforded a white solid, which was dissolved in Et_2O and dried over anhydrous $MgSO_4$. Filtration and evaporation of the solvent afforded a white solid in

high mass yield. Analysis of the product mixture by ^{29}Si NMR spectroscopy indicated that it contained mainly $[((c\text{-}C_6H_{11})SiO_{1.5})_2(c\text{-}C_6H_{11})(OH)SiO_{1.0})_4]_{\Sigma 6}$ (>60%) and $[((c\text{-}C_6H_{11})SiO_{1.5})_4(c\text{-}C_6H_{11})(OH)SiO_{1.0})_3]_{\Sigma 7}$ (>30%).

Preparation of $[((c\text{-}C_6H_{11})SiO_{1.5})_6((c\text{-}C_6H_{11})(OH)SiO_{1.0})_2]_{\Sigma 8}$ from $[((c\text{-}C_6H_{11})SiO1.5)_8]_{\Sigma 8}$: A solution of $[((c\text{-}C_6H_{11})SiO_{1.5})_8]_{\Sigma 8}$ (250 mg, 0.23 mmol) and 35% aqueous NEt4OH (0.1 mL, 0.25 mmol) in THF (3 mL) was stirred at room temperature for 1 h and then neutralized with an aqueous solution of HCl. The volatiles were evaporated in vacuo to afford a white solid, which was dissolved in Et_2O and dried over anhydrous $MgSO_4$. Filtration and evaporation of the solvent afforded a white microcrystalline solid in high yield. Analysis by ^{29}Si NMR spectroscopy and electrospray MS indicated that the product mixture contained ~76% (by ^{29}Si NMR) $[((c\text{-}C_6H_{11})SiO_{1.5})_6((c\text{-}C_6H_{11})(OH)SiO_{1.0})_2]_{\Sigma 8}$: $^{29}Si\{^1H\}$ NMR (99.3 MHz, C_6D_6, 25 °C) δ -60.4, -67.2, -69.8 (s, 1:1:2), as well as smaller amounts of unreacted $[((c\text{-}C_6H_{11})SiO1.5)_8]_{\Sigma 8}$ (δ -68.2, ~20%). Small ^{29}Si NMR resonances attributable to tetrasilanol $[((c\text{-}C_6H_{11})SiO_{1.5})_6((c\text{-}C_6H_{11})(OH)SiO_{1.0})_2]_{\Sigma 8}$ were also observed, as well as prominent peaks in the electrospray mass spectrum for the $[((c\text{-}C_6H_{11})SiO_{1.5})_6((c\text{-}C_6H_{11})(OH)SiO_{1.0})_2]_{\Sigma 8}$ (1117.36 for the ion with H+ and 1139 for the ion with Na+). Spectroscopic data for $[((c\text{-}C_6H_{11})SiO_{1.5})_6((c\text{-}C_6H_{11})(OH)SiO_{1.0})_2]_{\Sigma 8}$ matched the data previously reported for this compound.

Preparation of $[((c\text{-}C_6H_{11})SiO1.5)_4((c\text{-}C_6H_{11})(OH)SiO1.0)_3]_{\Sigma 7}$ from $[((c\text{-}C_6H_{11})SiO1.5)_8]_{\Sigma 8}$: A solution of $[((c\text{-}C_6H_{11})SiO1.5)_8]_{\Sigma 8}$ (500 mg, 0.46 mmol) and 35% aqueous NEt4OH (0.2 mL, 0.49 mmol) was refluxed in THF (5 mL) for 4 h then neutralized with dilute aqueous HCl. Evaporation of the volatiles afforded a white solid, which was dissolved in Et2O and dried over anhydrous MgSO4. Filtration and evaporation of the solvent afforded $[((c\text{-}C_6H_{11})SiO1.5)_4((c\text{-}C_6H_{11})(OH)SiO1.0)_3]_{\Sigma 7}$ as a white microcrystalline solid in 23% yield. Spectroscopic data for the product matched the data previously reported for samples of $[((c\text{-}C_6H_{11})SiO1.5)_4((c\text{-}C_6H_{11})(OH)SiO1.0)_3]_{\Sigma 7}$ obtained via the hydrolytic condensation of $c\text{-}C_6H_{11}SiCl_3$.

Preparation of $[((c\text{-}C_6H_{11})SiO1.5)_2((c\text{-}C_6H_{11})(OH)SiO1.0)_4]_{\Sigma 6}$ from $[((c\text{-}C_6H_{11})SiO1.5)]_{\Sigma 8}$: A solution of $[((c\text{-}C_6H_{11})SiO1.5)]_{\Sigma 8}$ (200 mg, 0.24 mmol) and 35% aqueous NEt4OH (0.2 mL, 0.49 mmol) in THF (5 mL) was stirred at 25 °C for 1 h then neutralized with dilute aqueous HCl. Evaporation of the volatiles afforded a white solid,

which was dissolved in Et_2O and dried over anhydrous $MgSO_4$. Filtration and evaporation of the solvent afforded $[((c\text{-}C_6H_{11})SiO_{1.5})_2((c\text{-}C_6H_{11})(OH)SiO_{1.0})_4]_{\Sigma 6}$ as a white solid in 63% yield (135 mg). $^{29}Si\{^1H\}$ NMR (99.3 MHz, $CDCl_3$, 25 °C) δ -59.4, -68.8 (s, 2:1). ^1H NMR (500 MHz, $CDCl_3$, 25 °C) δ 1.78 (v br m); 1.7 (v br m). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$, 25 °C) δ = 27.55, 27.47, 26.86, 26.62(CH_2); 23.68, 23.16 (2:1, SiCH). MS (ESI, 100% MeOH): *m/e* 846 ($M+H^+$, 48%); $M+Na^+$, 95%); 885 (M^+ - H + K, 100%).

Preparation of $[((C_6H_5CH=CH)SiO_{1.5})_6((C_6H_5CH=CH)(OH)SiO_{1.0})_2]_{\Sigma 8}$ from $[((C_6H_5CH=CH)SiO_{1.5})_8]_{\Sigma 8}$: A CH_2Cl_2/*i*-PrOH/THF(4/4/4 mL) solution of $[((C_6H_5CH=CH)SiO_{1.5})_8]_{\Sigma 8}$ (124.2 mg, 0.10 mmol) was added an aqueous solution of Et_4NOH (35%, 49.4 mL, 0.12 mmol) at –35 °C. After addition the resulting mixture was stirred at the same temperature for 5 h. The mixture was neutralized with 1N HCl solution and extracted with diethyl ether. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated. The residue was passed through a silica gel column using hexane/Et_2O (2:1) as an eluent. Evaporation of the volatiles gave pure $[((C_6H_5CH=CH)SiO_{1.5})_6((C_6H_5CH=CH)(OH)SiO_{1.0})_2]_{\Sigma 8}$ (112.4 mg, 0.09 mmol) as a white solid in 89% yield. ^1H NMR ($CDCl_3$) δ 5.83 (br s, 2H), 6.31-6.45 (m, 16H), 7.21-7.59 (m, 40H). ^{13}C NMR ($CDCl_3$) δ 117.41, 117.76, 117.96, 126.90, 128.43, 128.50, 128.53, 128.75, 128.83, 128.90, 137.17, 137.23, 137.29, 149.11, 149.15, 149.21. ^{29}Si NMR ($CDCl_3$) δ –78.05, –77.05,–68.66.

Preparation of $[((C_6H_5CH_2CH_2SiO_{1.5})_6((C_6H_5CH_2CH_2)(OH)SiO_{1.0})_2]_{\Sigma 8}$ from $[((C_6H_5CH_2CH_2)SiO_{1.5})_8]_{\Sigma 8}$: A CH_2Cl_2/*i*-PrOH/THF (5/5/5 mL) solution of $[((C_6H_5CH_2CH_2)SiO_{1.5})_8]_{\Sigma 8}$ (251.6 mg, 0.20 mmol) was added an aqueous solution of Et_4NOH (35%, 247.0 L, 0.60 mmol) at –35 °C. After addition the resulting mixture was stirred at the same temperature for 4 h. The mixture was neutralized with 1N HCl solution and extracted with diethyl ether. The organic layer was washed with brine, dried over $MgSO_4$, and evaporated. The residue was passed through a silica gel column using hexane/Et_2O (2:1) as an eluent. Evaporation of the volatiles gave pure $[((C_6H_5CH_2CH_2SiO_{1.5})_6((C_6H_5CH_2CH_2)(OH)SiO_{1.0})_2]_{\Sigma 8}$ (225.3 mg, 0.18 mmol) as a colorless oil in 88% yield. ^1H NMR ($CDCl_3$) δ 1.11-1.25 (m, 16H), 2.86-2.98 (m, 16H), 5.24 (br s, 2H), 7.25-7.47 (m, 40H). ^{13}C NMR ($CDCl_3$) δ 13.56, 14.19, 14.30, 28.90, 28.95, 28.98,

125.74, 125.84, 127.71, 127.83, 128.29, 128.33, 128.42, 143.67, 143.75, 143.78. ^{29}Si NMR ($CDCl_3$) δ –67.75, –65.99, –58.35.

Preparation of $[((CH_3C_6H_4SiO_{1.5})_6((CH_3C_6H_5)(OH)SiO_{1.0})_2]_{\Sigma 8}$ from $[((CH_3C_6H_5)SiO_{1.5})_8]_{\Sigma 8}$: A procedure similar to that used for $[((C_6H_5CH_2CH_2SiO_{1.5})_6((C_6H_5CH_2CH_2)(OH)SiO_{1.0})_2]_{\Sigma 8}$ was used to produce $[((CH_3C_6H_4SiO_{1.5})_6((CH_3C_6H_5)(OH)SiO_{1.0})_2]_{\Sigma 8}$. ^{1}H NMR ($CDCl_3$) δ 2.36 (s, 6H), 2.41 (s, 12H), 2.42 (s, 6H), 6.03 (br s, 2H), 7.08 (d, ^3J = 7.5 Hz, 4H), 7.16 (d, ^3J = 7.5 Hz, 8H), 7.24 (d, ^3J = 7.5 Hz, 4H), 7.56 (d, ^3J = 7.5 Hz, 4H), 7.62 (d, ^3J = 7.5 Hz, 8H), 7.72 (d, ^3J = 7.5 Hz, 4H). ^{13}C NMR ($CDCl_3$) δ 21.50, 21.53, 21.56, 127.10, 127.29, 127.65, 128.41, 128.48, 128.53, 134.25, 140.26, 140.31, 140.56. ^{29}Si NMR ($CDCl_3$) δ –78.22, –76.86,–69.05. MS (ESI, 100% MeOH): m/z Calcd for $C_{56}H_{58}O_{13}Si_8Na$ (100%): 1185.2. Found: 1185.4. $C_{56}H_{58}O_{13}Si_8H$ (20%): 1163.2. Found: 1163.5. $C_{56}H_{58}O_{13}Si_8K$ (20%): 1201.2. Found: 1201.3.

Preparation of $[(c\text{-}C_6H_{11}SiO_{1.5})_6((c\text{-}C_6H_{11})(OH)SiO_{1.0})_2]_{\Sigma 8}$ from $[(c\text{-}C_6H_{11}SiO_{1.5})_8]_{\Sigma 8}$: A THF (100 mL) solution of $[(c\text{-}C_6H_{11}SiO_{1.5})_8]_{\Sigma 8}$ (5.41 g, 5.00 mmol) was added a methanol solution of Me_4NOH (25%, 1.90 mL, 4.50 mmol) at room temperature. After addition the resulting mixture was stirred at the same temperature for 1 h. The mixture was neutralized with 1N HCl solution and extracted with diethyl ether. The organic layer was washed with brine, dried over $MgSO_4$, and evaporated. The residue was passed through a silica gel column using hexane and CH_2Cl_2 as an eluent. Evaporation of the volatiles gave pure $[(c\text{-}C_6H_{11}SiO_{1.5})_6((c\text{-}C_6H_{11})(OH)SiO_{1.0})_2]_{\Sigma 8}$ (4.60 g, 4.18 mmol) as a white solid in 84% yield. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 4.30 (br s, SiOH, 2H), 1.76 (br m's, 40H), 1.23 (br m's, 40H), 0.74 (br m's, 8H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 °C): δ 27.55, 27.48, 26.88, 26.79, 26.58, 26.53 (CH_2), 23.79, 23.69, 23.07 (4:2:2 for CH), ^{29}Si{^{1}H} NMR (99 MHz, $CDCl_3$, 25 °C): δ -59.91, -67.60, -69.85 (2:2:4). IR (25 °C, KBr, cm^{-1}): 2916, 2838, 1447, 1197, 1109. MS (70 eV, 200 °C, relative intensity): m/e 1015 ($[M - (C_6H_{11})]^+$, 100). Anal. Calcd for $C_{48}H_{90}O_{13}Si_8$ (found): C, 52.42 (52.32), H, 8.25 (8.68).

Reaction of $[((CH_3)_2CHCH_2)SiO_{1.5})_8]_{\Sigma 8}$ with NEt_4OH at room temperature. A solution of 35% NEt_4OH in water (0.11 mL, 0.25 mmol) was added to a THF (5 mL) solution of $[((CH_3)_2CHCH_2)SiO_{1.5})_8]_{\Sigma 8}$ (0.20 g, 0.23 mmol). The solution was stirred at room temperature for 1 h and then neutralized with an aqueous solution of HCl. The THF was removed in vacuo to afford a white oil, which was dissolved in Et_2O, dried over anhydrous $MgSO_4$ and filtered. Evaporation of the solvent afforded in 85% mass yield a milky white oil

containing (by ^{29}Si NMR spectroscopy and ESI MS) unreacted $[((CH_3)_2CHCH_2)SiO_{1.5})_8]_{\Sigma 8}$ (9%), $[((CH_3)_2CHCH_2)SiO_{1.5})_4((CH_3)_2CHCH_2)(OH)SiO_{1.0})_3]_{\Sigma 7}$ (29%), $[((CH_3)_2CHCH_2)SiO_{1.5})_6((CH_3)_2CHCH_2)(OH)SiO_{1.0})_2]_{\Sigma 8}$ (13%) and $[((CH_3)_2CHCH_2)SiO_{1.5})_4((CH_3)_2CHCH_2)(OH)SiO_{1.0})_4]_{\Sigma 8}$ (34%). Selected characterization data for $[((CH_3)_2CHCH_2)SiO_{1.5})_8]_{\Sigma 82}$: $^{29}Si\{^1H\}$ NMR (99.3 MHz, C_6D_6, 25 °C) δ -67.6; MS (ESI, 100% MeOH): *m/e* 873 ($M+H^+$, 5%). For $[((CH_3)_2CHCH_2)SiO_{1.5})_4((CH_3)_2CHCH_2)(OH)SiO_{1.0})_3]_{\Sigma 7}$: $^{29}Si\{^1H\}$ NMR (99.3 MHz, C_6D_6, 25 °C) δ -58.9, -67.1, -68.5 (3:1:3); MS (ESI, 100% MeOH): *m/e*: $_3$ 791 ($M+H^+$, 2%) and 813 ($M+Na^+$, 5%). For $[((CH_3)_2CHCH_2)SiO_{1.5})_6((CH_3)_2CHCH_2)(OH)SiO_{1.0})_2]_{\Sigma 8}$: $^{29}Si\{^1H\}$ NMR (99.3 MHz, C_6D_6, 25 °C) δ -59.6, -66.8, -68.7 (1:1:2); MS (ESI, 100% MeOH): *m/e* 891 ($M+H^+$, 11%) and 913 ($M+Na^+$, 5%). For $[((CH_3)_2CHCH_2)SiO_{1.5})_4((CH_3)_2CHCH_2)(OH)SiO_{1.0})_4]_{\Sigma 8}$: $^{29}Si\{^1H\}$ NMR (99.3 MHz, C_6D_6, 25 °C) δ (-58.4, -56.6, -66.5, -68.3, 1:1:1:1); MS (ESI, 100% MeOH): *m/e* 909 ($M+H^+$, 15%) and 931 ($M+Na^+$, 100%).

Preparation of $[((CH_3)_2CHCH_2)SiO_{1.5})_4((CH_3)_2CHCH_2)(OH)SiO_{1.0})_3]_{\Sigma 7}$ from $[((CH_3)_2CHCH_2)SiO_{1.5})]_{\Sigma 8}$: A solution of $[((CH_3)_2CHCH_2)SiO_{1.5})]_{\Sigma 8}$ (400 mg, 0.46 mmol) and 35% aqueous NEt_4OH (0.2 mL, 0.49 mmol) was refluxed in THF (5 mL) for 4 h then neutralized with dilute aqueous HCl. Evaporation of the volatiles afforded a white resin, which was dissolved in Et_2O and dried over anhydrous $MgSO_4$. Filtration and evaporation of the solvent afforded crude $[((CH_3)_2CHCH_2)SiO_{1.5})_4((CH_3)_2CHCH_2)(OH)SiO_{1.5})_3]_{\Sigma 7}$ as a white resinous substance in 44% yield. Colorless crystals were obtained by recrystallization from acetonitrile/toluene. Selected characterization data for $[((CH_3)_2CHCH_2)SiO_{1.5})_4((CH_3)_2CHCH_2)(OH)SiO_{1.0})_3]_{\Sigma 7}$: $^{29}Si\{^1H\}$ NMR (99.3 MHz, C_6D_6, 25 °C) δ -58.5, -66.9, -68.3 (s, 3:1:3). ^1H NMR (500 MHz, C_6D_6, 25 °C) δ 2.21 (m, 7 H, -CH-); 1.24 (d, J = 6.6 Hz, 18 H, CH_3); 1.21 (d, J = 6.6 Hz, 18 H, CH_3); 1.17 (d, J = 6.6 Hz, 6 H, CH_3); 0.97 (d, J = 7.1 Hz, 6 H, CH_2); 0.95 (d, J = 7.1 Hz, 6 H, CH_2); 0.92 (d, J = 7.0 Hz, 2 H, CH_2). $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6, 25 °C) δ = 25.7 (s, CH_3); 25.6 (s, CH_3); 25.5 (s, CH_3); 24.1 (s, CH_2); 24.05 (s, CH_2); 24.0 (s, CH_2); 23.4 (s, CH); 23.0 (s, CH); 22.6 (s, CH). MS (ESI, 100% MeOH): *m/e* 791.16 ($M+H^+$, 80%); 813.08 ($M+Na^+$, 100%). A single crystal X-ray diffraction study was also performed.

Preparation of $[((CH_3)_2CHCH_2)SiO_{1.5})_6((CH_3)_2CHCH_2)(OH)SiO_{1.0})_2]_{\Sigma 8}$ from

$[((CH_3)_2CHCH_2)SiO_{1.5})_8]_{\Sigma 8}$: A reactor was charged with 2126g (2.438 moles) $[((CH_3)_2CHCH_2)SiO_{1.5})_8]_{\Sigma 8}$ and 20 L THF. A basic solution of Me_4NOH (48 mL, 25 wt %, in MeOH) and THF (4 L) was cooled to 0 °C and added slowly (3.5 hours) to the reaction followed by 1 hour of stirring. Product formation was monitored by HPLC and upon completion was quenched into 320 mL conc. HCl and 700 mL H2O at 0 °C. Evaporation of the resulting solution gave waxy solids, that were washed with water until a pH = 7 and recrystallized using acetone and acetonitrile to produce 1525 g (70% yld) of product at 98% purity. ^{1}H NMR ($CDCl_3$): 3.99 (2 H, 2 x OH, bs); 1.85 (8 H, 8 x CH, m); 0.95 (48 H, 16 x CH_3, m); 0.60 (16 H, 8 x CH_2, m). {^{1}H} ^{13}C NMR ($CDCl_3$): 25.80; 25.75; 25.65; 23.99; 23.93; 23.86; 23.07; 22.46. Note that the above procedure can be adapted to both continuous and batch production methods to produce the desired product higher yield and greater purity.

Preparation of $[((CH_3)_2CH_2CHCH_3CH_2)SiO_{1.5})_6((CH_3)_2CHCH_2)(OH)SiO_{1.0})_2]_{\Sigma 8}$ from $[((CH_3)_2CH_2CHCH_3CH_2)SiO_{1.5})]_{\Sigma n}$ n = 8, 10: A reactor was charged with 128.0 g (96.82 mmol $[((CH_3)_2CH_2CHCH_3CH_2)SiO_{1.5})]_n$ and 2080 mL THF. A basic solution 48 mL (25 wt %, in MeOH) of Me_4NOH was cooled to 0 °C and added to the reaction mixture over 45 minutes and stirred for an additional 1.5 hour. Reaction progress was monitored by HPLC and at completion the reaction was quenched into HCl (150 mL, 1 N) and hexane (500 mL) with rapid stirring over a period of 1 hour. The top layer was removed and evaporated to give 125.7 g (97 %) of the colorless liquid product. ^{1}H NMR ($CDCl_3$): 1.83 (9.3, bm); 1.27 (9.8, bm); 1.15 (10, bm); 1.00 (23, m); 0.89 (64 , s); 0.85 (7.7, s); 0.73 (8.1, bm); 0.58 (8.0, bm). {^{1}H} ^{13}C NMR ($CDCl_3$): 54.50; 54.37; 31.19; 30.22; 29.48; 25.59; 25.49; 25.30; 25.22; 25.00; 24.36; 24.29.

Preparation of $[((CH_3)_2CH_2CHCH_3CH_2)SiO_{1.5})_4((CH_3)_2CHCH_2)(OH)SiO_{1.0})_3]_{\Sigma 7}$ from $[((CH_3)_2CH_2CHCH_3CH_2)SiO_{1.5})]_{\Sigma n}$ n = 8, 10: A similar procedure to that reported above for $[((CH_3)_2CH_2CHCH_3CH_2)SiO_{1.5})_6((CH_3)_2CHCH_2)(OH)SiO_{1.0})_2]_{\Sigma 8}$ can be using LiOH in acetone to prepare an oily trisilanol product that contains 95% of two trisilanol species $[((CH_3)_2CH_2CHCH_3CH_2)SiO_{1.5})_4((CH_3)_2CHCH_2)(OH)SiO_{1.0})_3]_{\Sigma 7}$ and $[((CH_3)_2CH_2CHCH_3CH_2)SiO_{1.5})_6((CH_3)_2CHCH_2)(OH)SiO_{1.0})_3]_{\Sigma 9}$ ^{1}H NMR (500 MHz, $CDCl_3$): δ(ppm) 0.562 (m, 1 H), 0.755 (m, 1 H), 0.908 (s, 9 H), 1.002 (m, 3 H), 1.137 (m, 1 H), 1.303 (m, 1 H), 1.831 (m, 1 H), 6.240 (br, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ(ppm) 24.06, 24.51, 24.86, 25.44, 25.59, 25.65, 25.89, 29.65, 29.90, 30.64, 30.68, 31.59, 32.02, 54.28, 54.77; ^{29}Si NMR (99.4 MHz, $CDCl_3$): δ(ppm) -68.66, -68.43, -67.54, -67.32, -58.75, -57.99. EIMS: m/e 1382 (22%, $M^+(T_9)$ - iOct - H_2O), 1052 (100%, $M^+(T_7)$ - iOct - H_2O).

Preparation $[((CH_3CH_2)SiO_{1.5})_4((CH_3CH_2)(OH)SiO_{1.0})_3]_{\Sigma 7}$ from $[((CH_3CH_2)SiO_{1.5})]_{\Sigma 8}$: A solution of 35% NEt_4OH in water (0.2 mL, 0.49 mmol) was added to a THF (5 mL) solution of $[((CH_3CH_2)SiO_{1.5})]_{\Sigma 8}$ (0.41 g, 0.46 mmol). The solution was refluxed for 7 h and then neutralized with an aqueous solution of HCl. The THF was removed in vacuo affording a colorless oil, which is dissolved in Et_2O and dried over $MgSO_4$ anhydrous. Evaporation of the solvent in vacuo and crystallization from MeOH afforded $[((CH_3CH_2)SiO_{1.5})_4((CH_3CH_2)(OH)SiO_{1.0})_3]_{\Sigma 7}$ as a white solid. Selected characterization data: $^{29}Si\{^1H\}$ NMR (99.3 MHz, C_6D_6, 25 °C) δ = -56.4, -64.8, 65.9 (3:1:3MS (ESI, 100% MeOH): *m/e*: 595 ($M+H^+$, 100%); 617 ($M+Na^+$, 60%).

Preparation $[((CH_3)SiO_{1.5})_4((CH_3)(OH)SiO_{1.0})_3]_{\Sigma 7}$ from $[((CH_3)SiO_{1.5})_8]_{\Sigma 8}$: A THF (350 mL) suspension of $[((CH_3)SiO_{1.5})_8]_{\Sigma 8}$ (8.5 g, 15.83 mmol) was added an aqueous solution of Et_4NOH (35%, 6.51 mL, 15.83 mmol) at room temperature. After addition the resulting mixture was stirred at the same temperature for 20 h. The mixture was neutralized with 1N HCl solution and extracted with diethyl ether. The organic layer was washed with brine, dried over $MgSO_4$. Evaporation of the volatiles gave a white oil-like solid. Recrystallization of the white solid from a mixed solvent ($MeOH/H_2O$ = 2.5/1) afforded $[((CH_3)SiO_{1.5})_4((CH_3)(OH)SiO_{1.0})_3]_{\Sigma 7}$ (1.35 g, 2.72 mmol) as a white powder in 17% yield. ^1H NMR ($CDCl_3$) δ 0.13 (s, 9H), 0.14 (s, 3H), 0.15 (s, 9H), 6.11(s, 3H). ^{13}C NMR ($CDCl_3$) δ -4.50, -4.35. ^{29}Si NMR ($CDCl_3$) δ -65.70, -65.16,-55.84. Calcd for $C_7H_{24}O_{12}Si_7$: C, 16.92; H, 4.87. Found: C, 17.16; H, 4.89. MS (ESI, 100% MeOH): *m/e*: 496.96 ($M+H^+$, 100%); 518.86 ($M+Na^+$, 75%).

Preparation $[((c\text{-}C_6H_{11})SiO_{1.5})_4((c\text{-}C_6H_{11})(OH)SiO_{1.0})_3]_{\Sigma 7}$ from $[((c\text{-}C_6H_{11})SiO_{1.5})_7((H)\ SiO_{1.0})_1]_{\Sigma 8}$: A solution of $[((c\text{-}C_6H_{11})SiO_{1.5})_7((H)SiO_{1.0})_1]_{\Sigma 8}$ (460 mg, 0.46 mmol) and 35% aqueous NEt_4OH (0.2 mL, 0.49 mmol) was refluxed in THF (5 mL) for 5 h then neutralized with dilute aqueous HCl. Evaporation of the volatiles afforded a white solid, which was dissolved in Et_2O and dried over anhydrous $MgSO_4$. Filtration and evaporation of the solvent afforded a white microcrystalline solid in high yield. Analysis of the product mixture by ^{29}Si NMR spectroscopy indicated that the major product was $[((c\text{-}C_6H_{11})SiO_{1.5})_4((c\text{-}C_6H_{11})(OH)SiO_{1.0})_3]_{\Sigma 7}$; small amounts of $[((c\text{-}C_6H_{11})SiO_{1.5})]_{\Sigma 8}$ were also present.

Preparation $[((c\text{-}C_5H_9)SiO_{1.5})_4((c\text{-}C_5H_9)(OH)SiO_{1.0})_2]_{\Sigma 8}$ from $[(c\text{-}C_5H_9)SiO_{1.5}]_{\Sigma 8}$: A 12-L reactor equipped with a mechanical stirrer, addition pump and drying tube, was charged

with 443.4 g (457.2 mmol) $[(c\text{-}C_5H_9)SiO_{1.5}]_{\Sigma 8}$ and 6.0 L THF. A base solution of Me_4NOH (in MeOH., 25 wt %, 212 mL) and THF (1.4 L) was prepared and added slowly to the reaction mixture and this mixture was stirred for 3 hours. Upon completion of the reaction a mechanically stirred quench tank was charged with 65 mL conc. HCl and 500 mL water was cooled to 0 °C and the above reaction mixture was quenched. Evaporation and filtration of the resulting mixture gave $[((c\text{-}C5H9)SiO1.5)4((c\text{-}C5H9)(OH)SiO1.0)2]_{\Sigma 8}$ to produce 364 g (81 %) of white solids at 98% purity. ^1H NMR ($CDCl_3$): 4.63 (2 H, 2 x OH, bs); 1.72 (16 H, 8 x CH_2, m); 1.56 (16 H, 8 x CH_2, m); 1.46 (32 H, 16 x CH_2, m); 0.94 (8 H, 8 x CH, m). $\{^1H\}$ ^{13}C NMR ($CDCl_3$): 27.41; 27.39; 27.36; 27.20; 27.06; 27.02; 27.00; 26.99; 22.88; 22.66; 22.16. Variations of this preparative method can be used to design both continuous and batch processes.

Although the present invention has been described above in terms of specific embodiments, it is anticipated that alterations and modifications thereof will no doubt become apparent to those skilled in the art. It is therefore intended that the following claims be interpreted as covering all such alterations and modifications as fall within the true spirit and scope of the invention.

What is claimed is:

CLAIMS

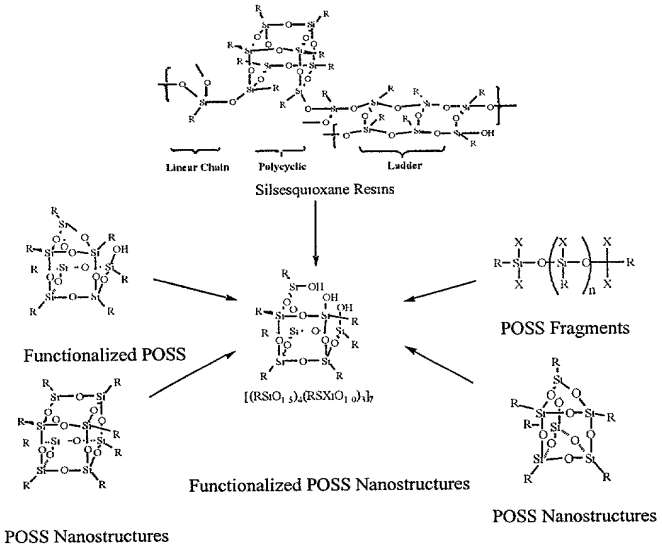
1. The process of using bases to convert polysilsesquioxane resins into POSS nanostructures of the type: homoleptic $[(RSiO_{1.5})_n]_{\Sigma\#}$, heteroleptic $[(RSiO_{1.5})_m(RSiO_{1.5})_n]_{\Sigma\#}$ and functionalized heteroleptic $[(RSiO_{1.5})_m(RXSiO_{1.0})_n]_{\Sigma\#}$. Where m and n represent the stoichiometric composition and # = the number of silicon atoms contained within the nanostructure (aka cage size).

2. The process of using bases to convert POSS fragments $[(RSiO_{1.5})_m(RXSiO_{1.0})_n]_{\Sigma\#}$ into POSS nanostructures of the type homoleptic $[(RSiO_{1.5})_n]_{\Sigma\#}$, heteroleptic $[(RSiO_{1.5})_m(RSiO_{1.5})_n]_{\Sigma\#}$ and functionalized heteroleptic $[(RSiO1.5)_m(RXSiO1.0)_n]_{\Sigma\#}$.

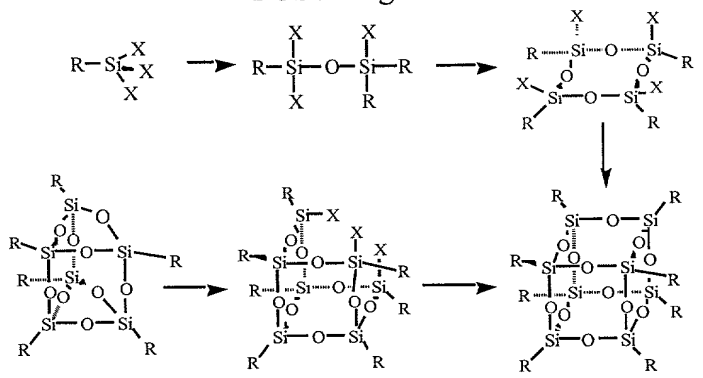
3. The process of using bases to convert POSS nanostructures homoleptic $[(RSiO1.5)n]_{\Sigma\#}$, heteroleptic $[(RSiO1.5)_m(RSiO1.5)_n]_{\Sigma\#}$ into functionalized heteroleptic $[(RSiO1.5)_m(RXSiO1.0)_n]_{\Sigma\#}$. POSS nanostructures.

4. The process of reacting POSS fragments with POSS and silicate nanostructures to form functionalized heteroleptic $[(RSiO1.5)_m(RXSiO1.0)_n]_{\Sigma\#}$, $[(XSiO1.5)_m(RXSiO1.0)_n]_{\Sigma\#}$. POSS nanostructures.

5. The process of directly manufacturing $[(RSiO1.5)_4(RXSiO1.0)_3]_{\Sigma7}$ from polysilsesquioxanes $[(RSiO1.5)n]_{\Sigma\#}$, nonfunctionalized $[(RSiO1.5)_m(RSiO1.5)_n]_{\Sigma\#}$ POSS cages, and POSS fragments $[(RSiO1.5)_m(RXSiO1.0)_n]_{\Sigma\#}$ using base as shown in the figure.



6. The process for the sequential growth of POSS fragments, homoleptic $[(RSiO_{1.5})_n]_{\Sigma\#}$, heteroleptic $[(RSiO_{1.5})_4(RXSiO_{1.0})_3]_{\Sigma 7}$ POSS nanostructures from POSS fragments using base, as shown in the figure.



POSS Nanostructures and Functionalized POSS Nanostructures

7. The compositions reported in the examples for homoleptic $[(RSiO_{1.5})_n]_{\Sigma\#}$, heteroleptic $[(RSiO_{1.5})_m(RSiO_{1.5})_n]_{\Sigma\#}$ and functionalized heteroleptic $[(RSiO_{1.5})_m(RXSiO_{1.0})_n]_{\Sigma\#}$ POSS and POSS silicate nanostructures.

ABSTRACT

Three processes for the manufacture of polyhedral oligomeric silsesquioxanes (POSS) which utilize the action of bases that are capable of either attacking silicon or any compound that can react with a protic solvent (e.g. ROH, H_2O etc.) and generate hydroxide $[OH]^-$, alkoxide $[RO]^-$, etc. The first process utilizes such bases to effectively redistribute the silicon-oxygen frameworks in polymeric silsesquioxanes $[RSiO_{1.5}]_\infty$ where ∞ = 1–1,000,000 or higher into POSS nanostructures of formulas $[(RSiO_{1.5})_n]_{\Sigma\#}$, homoleptic, $[(RXSiO_{1.5})_n]_{\Sigma\#}$, functionalized homoleptic, $[(RSiO_{1.5})_m(R'SiO_{1.5})_n]_{\Sigma\#}$, heteroleptic, and $\{(RSiO_{1.5})_m(RXSiO_{1.0})_n\}_{\Sigma\#}$, functionalized heteroleptic nanostructures. The second process utilizes base to aid in the formation of POSS nanostructures of formulas $[(RSiO_{1.5})_n]_{\Sigma\#}$ homoleptic and $[(RSiO_{1.5})_m(R'SiO_{1.5})_n]_{\Sigma\#}$ heteroleptic and $[(RSiO_{1.5})_m(RXSiO_{1.0})_n]_{\Sigma\#}$ functionalized heteroleptic nanostructures from silanes $RSiX_3$ and linear or cyclic silsesquioxanes of the formula $RX_2Si\text{-}(OSiRX)_m\text{-}OSiRX_2$ where m = 0-10, X = OH, Cl, Br, I, alkoxide OR, acetate OOCR, peroxide OOR, amine NR_2, isocyanate NCO, and R. The third process utilizes base to selectively ring-open the silicon-oxygen-silicon (Si-O-Si) bonds in POSS structures to form POSS species with incompletely condensed nanostructures. These processes also afford stereochemical control over X. The three processes result in new POSS species that can undergo additional chemical manipulations to ultimately be converted into POSS-species suitable for polymerization, grafting, or other desirable chemical reactions.

RULE 63 (37 C.F.R. 1.63)
DECLARATION AND POWER OF ATTORNEY FOR PATENT APPLICATION
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

As a below named inventor, I hereby declare that my residence, post office address and citizenship are as stated below next to my name, and I believe I am an original, first and joint inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled **PROCESS FOR THE FORMATION OF POLYHEDRAL OLIGOMERIC SILSESQUIOXANES**, the specification of which was filed in the U.S. Patent Office on August 4, 2000 under Serial No. _____.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose all information known to me to be material to patentability as defined in 37 C.F.R. 1.56. I hereby claim foreign priority benefits under 35 U.S.C. 119/365 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate filed by me or my assignee disclosing the subject matter claimed in this application and having a filing date (1) before that of the application on which priority is claimed, or (2) if no priority claimed, before the filing date of this application:

PRIOR FOREIGN APPLICATION(S): Number	Country	Day/MONTH/Year Filed	Date first Laid-open or Published	Date Patented or Granted	Priority Claimed
					Yes ☐ No ☐

I hereby claim domestic priority benefit under 35 U.S.C. 119/120/365 of the indicated United States applications listed below and PCT international applications listed above or below and, if this is a continuation-in-part (CIP) application, insofar as the subject matter disclosed and claimed in this application is in addition to that disclosed in such prior applications, I acknowledge the duty to disclose all information known to me to be material to patentability as defined in 37 C.F.R. 1.56 which became available between the filing date of each such prior application and the national or PCT international filing date of this application:

PRIOR U.S. PROVISIONAL, NONPROVISIONAL AND/OR PCT APPLICATION(S) Application No.:	Day/MONTH/Year Filed:	Status pending, abandoned, patented)	Priority Claimed?
60 /147,435	4 August 1999		Yes ☑ No ☐

and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

And I hereby appoint Pillsbury Madison & Sutro LLP, 2550 Hanover Street, Palo Alto, CA 94304-1115, telephone number (650) 233-4500 (to whom all communications are to be directed), and the below-named persons (of the same address) individually and collectively my attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith and with the resulting patent, and I hereby authorize them to delete persons no longer with their firm and to act and rely on instructions from and communicate directly with the person/assignee who first sent this case to them and by whom I hereby declare that I have consented after full disclosure to be represented unless/until I instruct the above Firm and/or a below attorney in writing to the contrary.

Paul N. Kokulis	16773	Dale S. Lazar	28872	Timothy J. Klima	34852	W. Patrick Bengtsson	32456
Raymond F. Lippitt	17519	Glenn J. Perry	28458	Stephen C. Glazier	31361	Jack S. Barufka	37087
G. Lloyd Knight	17698	Kendrew H. Colton	30368	Paul F. McQuade	31542	Adam R. Hess	41835
Carl G. Love	18781	Paul E. White, Jr.	32011	Ruth N. Morduch	31044	William P. Atkins	38821
Kevin E. Joyce	20508	G. Paul Edgell	24238	Richard H. Zaitlen	27248	Paul L. Sharer	36004
George M. Sirilla	18221	Lynn E. Eccleston	35861	Roger R. Wise	31204	**DAVID H. JAFFER**	**32243**
Donald J. Bird	25323	David A. Jakopin	32995	Jay M. Finkelstein	21082		
Peter W. Gowdey	25872	Mark G. Paulson	30793	Michael R. Dzwonczyk	36787		

1. INVENTOR'S SIGNATURE: _____ Date _____
Inventor's Name **Joseph D. LICHTENHAN**
Residence (City, State): **San Juan Capistrano, California**
Post Office Address: **31085 Via Sonora, San Juan Capistrano, CA 92675**
Country of Citizenship: United States of America

2. INVENTOR'S SIGNATURE: _____ Date _____
Inventor's Name: **Joseph J. SCHWAB**
Residence (City, State): **Huntington Beach, California**
Post Office Address: **16352 Bradberry, Huntington Beach, CA 92647**
Country of Citizenship: United States of America

3. INVENTOR'S SIGNATURE: _____ Date _____
Inventor's Name **Yi-Zong AN**
Residence (City, State): **Fountain Valley, California**
Post Office Address: **16425 Harbor Boulevard, Apt. 224, Fountain Valley, CA 92708**
Country of Citizenship: United States of America

4. INVENTOR'S SIGNATURE: ______________________________ Date ______________________________
Inventor's Name: **William REINERTH**
Residence (City, State): **Westminster, California**
Post Office Address: **7051 Natal Drive, Apt. 25, Westminster, CA 92683**
Country of Citizenship: United States of America

5. INVENTOR'S SIGNATURE: ______________________________ Date ______________________________
Inventor's Name **Michael J. CARR**
Residence (City, State): **Fountain Valley, California**
Post Office Address: **9565 Slater Avenue, Fountain Valley, CA 92708**
Country of Citizenship: United States of America

6. INVENTOR'S SIGNATURE: ______________________________ Date ______________________________
Inventor's Name: **Frank J. FEHER**
Residence (City, State): **Costa Mesa, California**
Post Office Address: **3210 Montana Avenue, Costa Mesa, CA 92626**
Country of Citizenship: United States of America

7. INVENTOR'S SIGNATURE: ______________________________ Date ______________________________
Inventor's Name **Raquel TERROBA**
Residence (City, State): **Irvine, California**
Post Office Address: **15610 Tustin Village Way, Apt. 27, Fountain Valley, CA 92708**
Country of Citizenship: United States of America